공학박사학위논문

# Application of Coffee Ground and Woodchip Biochars as a Soil Amendment for Crop Cultivation

커피 찌꺼기와 우드칩 바이오차가 토양
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서울대학교 대학원

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# Application of Coffee Ground and Woodchip Biochars as a Soil Amendment for Crop Cultivation

by

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# Abstract

# Application of Coffee Ground and Woodchip Biochars as a Soil Amendment for Crop Cultivation

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Crop wastes and biomass from feedstocks cause significant environmental problems and have negative consequences for humans. If used correctly, biomass residues contain a great deal of energy potential. Most crop wastes, particularly agricultural leftovers, may be transformed to biochar utilizing thermodynamic technologies such as a muffle furnace. The derivation of wastes for useful materials as well as biochars is the key tool to helps in controlling and handling of biomass in the area or sites. Generally, the operator at temperature at 400 ˚C to make biochar with fixed carbon contents ranging 52.45, and 78% respectively. Biochar conductions into soil amendment for improving the physicochemical and biological properties of the soil owing to biochar's high organic carbon content, which increases the amount of nutrients in the soil and activates it as a carbon sequestration agent over time. Biochar, in and of itself, is a nutrient source that may affect soil nutrient stores and bioavailability, as well as the microbial community and the environment.

The majority of nitrogen (N) in the agricultural system is absorbed by plants through ammonium ($NH_4^+$) or nitrate ($NO_3^-$). Ammonium is released through mineralization process while $NO_3^-$ is a product of nitrification process through $NH_4^+$ oxidation. This method has two parts: (i) $NH_4^+$ was transformed to nitrate ($NO_2^-$) through ammonia-oxidizing bacteria; (ii) $NO_2$ was changed to $NO_3$ via nitrite-oxidizing bacteria. Increased nitrate ($NO_3$) leakage into waterbodies has made nitrogen losses from fertilizer techniques a significant environmental problem across the world in recent years. Nutrient leaching is a concern not just for soil function and plant uptake, but it may also lead to nutrient enrichment and eutrophication in water, both of which are harmful to human health. Human absorption of excess $NO_3$, for example, can cause newborn methemoglobinemia and a variety of malignancies. As a result, eliminating excess inorganic N from soil solutions or waterbodies has major ecological and societal consequences. Much further, various physical, chemical, and biological techniques for regulating inorganic nitrogen in the aqueous phase have been presented, with adsorption utilizing biochar being one of the most popular.

The primary objective of this research was to demonstrate the application of biochar and the effect of long-term exposure to coffee ground and woodchip biochars on Pak Choi cultivation in sandy loam soil: (1) to predict the potential advantages of biochar when surplus nitrogen fertilizers are applied through adsorption (Park M. H. et al., 2019) and desorption of macronutrients in the aqueous phase; (2) to study the effect of biochar (biochar-soil mixture) on inorganic nitrogen (N) and plant growth production under plot conditions in the soil phase. (3) to investigate the properties of biochars and microbiology under long-term exposure or aging in the soil environment and (4) to verify biochar effects on crop growth and yield in plot experiment. It is also necessary to study the effect of biochar production on $NH_4^+$-N

and $NO_3^-$-N adsorption and desorption to quantitatively explain the relative effect of aging biochar ($NH_4^+$-N and $NO_3^-$-N) on Pak Choi Yields. Furthermore, the kinetics model experiment was important in determining the releasing properties after equilibrium, as well as the long-term exposure characteristics of nitrogen were obtained.

The initial pH of soil (6.55) is in a proper range for plant nutrient uptake whereas the initial pH of coffee grounds biochar (CBC), and woodchips biochar (WBC) varied from moderately alkaline to alkaline. CBC and WBC produced similar yields which varied from about 32.49% to 33.93% by weigh, respectively. The percentage of ash content in CBC (2.9%) was lower than ash content in WBC (11.6%), however, its ash contents were in the average ranges. C/N ratio, ranging from about 52 for CBC and 312 for WCB, respectively. CBC and WBC had O/C and H/C ratios close to the recommendation thresholds, indicating well-pyrolysed ranges, enrichment of aromatic structures, and prone to degradation. The CEC of biochars were similar and were in the average ranges while CEC of the initial soil was in suitable for soil to hold and exchange cations in the soil solution, however, main elements in CBC, WBC, and the initial soil were exchangeable Ca, K, Mg, and Na, respectively. The similar strong peaks decreased at ~1,350 $cm^{-1}$ and ~1,600 $cm^{-1}$ of C=C and –COOH for both CBC and WBC were due to carbon condensation. BET specific surface area of biochars of CBC and WBC were large, this showed that SEM of WBC has more chance to enhance exposure of inorganic minerals as it increased in the pore structure comparing to CBC. The Langmuir isotherm model suited the ammonium nitrogen ($NH_4^+$-N) adsorption to both CBC and WBC biocahrs better than the Freundlich isotherm model, with higher $r^2$ values. In comparison to CBC, WBC emitted more nitrogen from the surface. The pseudo-first order and pseudo-second order kinetic models fit better $NH_4^+$-N and $NO_3^-$-N adsorption, respectively. As a result, we concluded that both biochar products can be used in situations where $NH_4^+$-N adsorption is a problem, while CBC can be used in situations where $NO_3^-$-N desorption is a problem. However, more study on using biochars to reduce $NO_3^-$-N pollution is required.

**Keyword :** Biohcars, Coffee Ground, Crop, Heavy Metal, $NH_4^+$-N, $NO_3^-$-N, Microbial Community, Pyrolysis, Woodchip.

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# Table of Contents

## Chapter 1.

## Chapter 2.

## Chapter 3.

## Chapter 6

# List of Tables

# List of Figures

# CHATPER 1.

# INTRODUCTION

## 1.1. General overview

Agriculture is responsible for feeding the world's ever-growing population, and farmers must continually maintain and improve soil quality in order to meet expanding food demand (FAO, 2017). Biochar is a finely pyrolyzed organic substance that has been proposed as a substitute for plant nutrients in order to increase and sustain soil productivity. It possesses particular physical and chemical capabilities that allows it to function as an absorbent, including a porous structure with enhancement the moisture contents by treated soils (Laird, and Pietikäinen, 2000), as well as an increase in nutrient storage capacity (Glaser et al., 2002). The amount of exchangeable cations and carboxylic groups in biochar has increased as well as a large surface area, is responsible for enhancing the nutrient retention capacity of soils (Ding et al., 2016). As a substrate, biochar may be made from any naturally occurring feedstock. The feedstock must be thermally carbonized in order to produce biochar. Pyrolysis is a thermodynamic reaction in which feedstock is cooked to high temperatures while being oxygen-depleted. The end result is a carbonized black substance that may be utilized as a soil amendment. Pyrolysis is essential in the formation of biochar because it traps carbon (C) in a more refractory form known as the black carbon. The quality of biochar is influenced not only by the biomass used, but also by pyrolysis parameters including heat and contact time (Laird et al., 2009; Manyà., 2012). Based on the precursor and production conditions, the biochar result has unique features. The temperature of biochar pyrolysis, for example, can have a direct impact on nutrient retention. Because biochar is made at temperature of 400 degrees celsius, it has increased the ration of Hydrogen/Carbon and increased Oxygen/Carbon, and also surface area. However, it has a low Hydrogen/Carbon ratio, low oxygen concentration, and a larger surface area when the temperature is above 700 degrees Celsius (Aghoghovwia, Makhosazana P. 2018).

One of the most significant strategies for preventing global climate change and its implications for living beings is carbon sequestration. Because biochar is projected to endure hundreds to thousands of years in the soil, it is becoming increasingly attractive as a soil supplement to permanently store carbon (Aghoghovwia, Makhosazana P. 2018). In other studies, biochar has been found to increase soil fertility in sandy and highly worn soils, and its usage as a soil supplement has the added benefit of preventing nitrogen fertilizer contamination by encouraging fertilizer preservation (Sohi., 2010).

Biochars may absorb nutrients from applied fertilizers, according to recent study, and these nutrients can occasionally be released reversibly. Biochar may be ideal for use as a slow-release fertilizer due to its characteristic (Ding et al., 2016). Different types of Oak wood wastes and converted biochar absorbed 81 and 75 percent of ammonium ($NH_4^+$) in a research study, respectively. Biochar is produced at temperatures of 400 and 600 degrees Celsius (Zhang et al., 2015). The mechanism for $NH_4^+$ adsorption has been proposed as electron donor-acceptor interaction, in which condensed aromatic carbon rings react with ammonia (Aghoghovwia, Makhosazana P., 2018). The biochar was prepared at 600 and 400 degrees Celsius and then desorbed with 2 M potassium chloride (KCl) solution (Aghoghovwia, Makhosazana P., 2018). It also contained 18% and 31% $NH_4^+$-N, respectively.

According to the researchers, biochar formed at temperatures more than 400 °C was more efficient in sorbing organic and inorganic pollutants than biochar generated at lower temperatures due to its large surface area and unique micropores (Uchimiya et al., 2010; Ding Yang et al., 2016).

Pine wood biochar has also been demonstrated to substantially minimize inorganic nitrogen (N) fertilizer leaching from sandy soils. Biochar is a porous material with a high cation exchange capacity (CEC), which is one of the reasons for its high nutrient retention capacity. This is necessary for minimizing pollution produced either by leaching from chemical fertilizers into the environment (Aghoghovwia, Makhosazana P., 2018). Biochar, on the other hand, was shown to reduce the quantity of exchangeable inorganic nitrogen in sandy soil, notably nitrate. The current study examined four distinct biochar production methods in order to better understand how biochar might behave differently depending on the feedstock and pyrolysis conditions. Individual biochars' nutrient sorption characteristics, nutrient cycling potential, and other features (Yao et al., 2012; Gaskin et al., 2008).

Biochar has an impact on soil carbon and nitrogen mineralization rates because it limits the C and N pools that microorganisms may use. When nitrogen is introduced to the soil, the C/N ratio of biochar determines whether it will be mineralized or immobilized (Aghoghovwia, Makhosazana P., 2018). When new biochars with a high C/N ratio are exposed to microbial degradation, N removal from the soil is decreased, and the likelihood of success increases (Bruun et al., 2012). Due to smaller levels of labile C, biochar in soils has lower carbon dioxide-C respiration rates than the control (Lehmann et al., 2011). We needed to investigate biochar properties since they influence soil C and N mineralization.

Low CEC is usually associated with low soil organic carbon (SOC) levels and the presence of kaolinitic clays with low activity (Lal R., 2005). According to the study, biochar may improve soil electrical conductivity by 124.6 percent, cation exchange capacity by 20 perent, and soil acidity by 31.9 percent (Ding Yang et al., 2016). Biochar has also been proven to be a successful approach for improving crop productivity in acidic sandy soils, carbon sequestration in soils, and long-term carbon storage in other research investigations (Alkharabsheh Hiba M et al., 2021).

The impact of reduced nitrogen leaching and release on biochar applications in soils is well understood (Sika and Hardie., 2014). However, the processes through which biochar, soils, and fertilizers interact to improve production and long-term exposure or aging in soil remain unknown (Aghoghovwia, Makhosazana P., 2018). Additionally, while biochar may be made from a number of sources, the feedstocks employed in this study were coffee ground and woodchip, as well as pyrolysis conditions to create the biochars. Although different feedstocks, pyrolysis conditions, and single plant cultivation are used, the effects are generally unknown.

## 1.2. Research objectives

The study's main objective was to assess biochar generated from various feedstocks and their impacts on nitrogen in sandy loamy soil utilizing various feedstocks and pyrolysis conditions. The study's specific aims were as follows:

| | |
|---|---|
| 1) | To predict the potential advantages of biochars when surplus Nitrogen fertilizer is applied.<br>To use the batch test of adsorption and desorption to predict surplus fertilizers conditions. |
| 2) | To investigate the effect of biochar (biochar-soil mixture) on inorganic nitrogen (N) and crop growth production under plot conditions in the soil phase. |
| 3) | To investigate the property change of biochar, and microbiology under long-term exposure in the soil environment.<br>To verify biochar effect on crop growth and yield in plot conditions. |

## 1.3. Dissertation structure

As shown in Figure 1.1, the dissertation is divided into six chapters. Chapter 1 provides a basic overview of biochar and it also discusses the study's motivation. Chapter 2 provides an overview of the foundational literature for this study. The adsorption and desorption were shown in Chapter 3. In Chapter 3, the two forms of biochar materials are characterized in terms of their physical and chemical properties. This study's methodology was mostly based on scholarly literature. In Chapter 4, an adsorption-desorption experiment is used to analyze the features discovered during the biochar characterisation. This research focuses on biochar's ability to adsorb and desorb mineral N from solution and using $NH_4Cl$ and $KNO_3$. The effects of long-term biochar application on C and N mineralization and soil physical changes at the biochar surface are examined in Chapter 5. The SNU loop application test was used to investigate the effects of two biochar soil supplements, fresh and aged coffee grounds and wood chip biochar, on release, leachate, and thread mineral N availability in sandy loam soil. The reports, as well as the general perspective of the research, are summarized in Chapter 6.

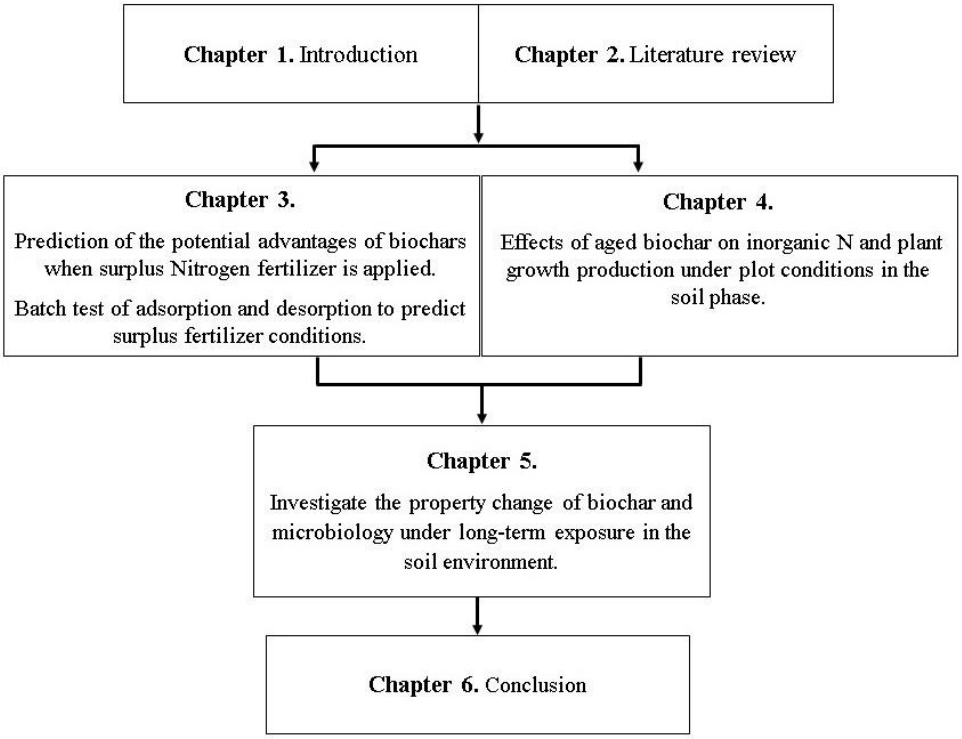

**Figure 1.1.** Dissertation's structure

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# CHATPER 2

# LITERATURE REVIEW

## 2.1. Introduction

Although there was no influence on grain output after the fourth year of wood biochar application under these conditions, the rise in soil organic carbon with biochar rate implies that biochar may indirectly enhance soil organic carbon storage in the long run by increasing plant biomass. Biochar, when used in combination with other sustainable soil management techniques such as cover crops or green manures, has the potential to increase soil resilience (Madari Beata E. et al., 2017). The first chemical change that occurs when biochar is introduced to soil is an elevation in pH, indicating that biochar adds lime to the soil. When utilized as an amendment, biochar is both physiologically and microbiologically sustainable.

Furthermore, biochar has also been found to reduce nutrient losses, particularly nitrate, a highly dynamic macronutrient (e.g. N, P, K) due to (Aghoghovwia, Makhosazana P. 2018), as well as the absorption of potentially hazardous elements (Laird et al., 2010b; Sika and Hardie, 2014).

According to Lehmann and Josepth (2019), biochar must meet two criteria in order to contribute to climate change mitigation. The first is that vegetative biomass had to be grown at the same time it was pyrolyzed. Because photosynthesis is the process through which plants convert $CO_2$ from the atmosphere into organic C. Importantly, coffee residues and biochar products were studied to see whether there were any agronomic or environmental benefits that could improve soil quality (Domingues R. R.et al., 2017). In addition, several research used a combination of coffee grind with compost or fertilizer, as well as other elements like bark (Wakasawa et al., 1998b). The effects of applying coffee ground biochar alone on crop development and yields are limited. Similarly, woodchip biochar substances are rich in nutrients and have a significant potential for increasing C storage in tropical soils due to their greater aromatic character and high C concentration (Domingues R. R. et al., 2017). We don't have any comparative data on the use of coffee grounds and woodchip biochar on a single green vegetable.

Pak Choi is one of the most popular vegetable in the kitchen of Cambodia. According to past research, Pak Choi has a variety of nutrients such as carotenoids, vitamins C, E, and K, folate, and minerals, all of which are useful in reducing the risk of cancer in humans (Hecht et al., 2000). However, the productivity of Pak Choi is limited in Cambodia owing to low soil fertility.

## 2.2. Biomass for pyrolysis

According to the findings, each component of plant biomass (Aghoghovwia, Makhosazana P. 2018), degrades at different rates and through different pathways during pyrolysis, with cellulose having the strongest O-H and C-O stretches, (Aghoghovwia, Makhosazana P. 2018), hemicelluloses with the largest C=O compounds, and lignin with the highest methoxyl-O-CH3, C-O-C stretching, and aromatic ring containing compounds, and lignin with the largest methoxyl-O-CH3, C-O-C stretching, and aromatic ring containing compounds, and lignin with the largest methoxyl-O-CH3, C-O-C stretching, and aromatic ring containing compounds, and lignin (Bridgwater et al., 1999; Yang et al., 2007; Aghoghovwia, Makhosazana P. 2018).

Biochar can be produced by pyrolyzing organic material. Agricultural wastes such as chicken litter and peanut hulls, rice husk, rice straw, forestry wastes like pine, sugarcane, and sewage sludge have all been investigated and converted into biochar (Gaskin and Fu et al., 2011; Jindo et al., 2014; Conte et al., 2014; Gaskin et al., 2008; Alburquerque et al., 2014; Yuan et al., 2013; Srinivasan et al., 2015). Pyrolysis of biomass has a clear positive knock-on effect in that it helps to reduce and utilize waste that would otherwise be thrown.

The degree of reactivity of the biochar produced is determined by the chemical composition of the starting organic biomass (Aghoghovwia, Makhosazana P. 2018). During the thermal decomposition of feedstock's and elemental content changes structurally, physically, and chemically. Aromatic structures and furan-like molecules are destroyed first, followed by cellulose and lignin structures. (Baldock and Smernik, 2002; Paris et al., 2005) Because pyrolysis transforms aliphatic C to aromatic C, organic C mineralization rates are reduced (Chan and Xu 2009).

## 2.3. Pyrolysis

Hemicellulose, celluloses, and lignin undergo structural modifications during pyrolysis. The impact and condition of the final biochar product, including temperature (Lua., 2004; Brown., 2006). Organic compounds lose their chemically bonded moisture when temperatures above 120 °C.

Biochar is made from the pyrolysis charcoal that has been crushed into tiny pieces and put to the soil. Bio-oil is a mixture of polar organics and water that is both hydrophilic and oleophobic (Aghoghovwia, Makhosazana P. 2018). Pyrolysis produces biochars which can be used in a variety of ways. This could be used as a energy in industrial boilers. Biogas (also known as syngas) is a renewable energy source that may be utilized to create electricity. Bio-oil and charcoal may both be utilized as fuels or feedstocks, and the gas can be recycled. As a result, because pyrolysis generates no waste (Mohan et al., 2006).

The materials and techniques employed in pyrolysis determine the amount and quality of charcoal, bio-oil, and biogas produced (in terms of shape, structure, and characteristics) (Aghoghovwia, Makhosazana P. 2018). The biomass feedstock is referred to as the materials, and it has a major influence on the initial characteristics of biochar (Gaskin et al., 2008). The pyrolysis parameters (peak temperature, duration, heating rate, etc.) that result in pyrolysis products like biochar with varied physico-chemical characteristics are referred to as the method (Brown 2009). Traditional ways of manufacturing biochar have been superseded by automated systems, which have the advantage of being far more energy efficient than traditional kilns. Due to the fact that pyrolysis circumstances vary, there is no definitive description of the various pyrolysis procedures in terms of specific pyrolysis peak temperatures, particle residence times, heat transmission, or heating rates. As a result, the terminology used to describe different pyrolysis procedures is amorphous and arbitrary (Aghoghovwia, Makhosazana P. 2018).

### 2.3.1. Slow pyrolysis

Slow pyrolysis is a common pyrolysis technique that is used to produce charcoal. It can be done in batch systems called charcoal kilns or in continuous systems like drum pyrolyzers or screw pyrolyzers. According to the pyrolysis temperature at 300 degrees Celsius, alkalinity dropped 9.4, 8.6, and 7.7% (Ding Yang et al., 2010; Lehamann, et al., 2015). They utilize gradual heating of biomass to temperatures of 400 °C in an anoxic environment and the temperature at 500 °C being the optimum temperature (Lee et al., 2013). Thorough pyrolysis, biochar formation was reduced danger of immobilization occur from a relatively lengthy biomass residence period during slow pyrolysis (Bruun et al., 2012). Long solid and gas particle residence times, ranging from the few minutes to many hours, have been observed (Aghoghovwia, Makhosazana P. 2018), are additional characteristics of slow pyrolysis (Mohan et al., 2006). Researchers discovered that biochar produced at temperatures greater than 400 degrees Celsius was more effective for organic and inorganic pollutant sorption than biochar produced at lower temperatures. This was due to the large surface area of the biochar as well as the substantial micropore development (Uchimiya et al., 2010; Ding Yang et al., 2016). Surface and micro porosity, as well as CEC, were improved by pyrolysis at 600 °C, although volatile materials were lost.

### 2.3.2 Fast pyrolysis

The most significant distinction is that rapid pyrolysis technology is generally more sophisticated than slow pyrolysis technology, owing to the fact that bio-oil production, rapid pyrolysis technique is ideal. A well-written description of the operating concept of rapid pyrolysis may be found in (Aghoghovwia, Makhosazana P. 2018). Due to the charring is the result of slow pyrolysis (low heating rate and extended residence time) under slow process conditions. Pyrolysis is a rapid process that involves high temperatures of around 1000 ° C per minute and a pyrolysis temperature of around 500 °C, with an evaporation period of approximately < 2 s (Choi et al., 2017; D. Wang et al., 2020). Fast pyrolysis breaks down biomass particles quickly, releasing pyrolysis and biochemical gases (10-15% wt.). Greater pyrolysis temperatures are expected to limit biogas generation in order to allow stress release, and higher heating rates have a similar effect. The biomass is rapidly heated at high heating rates, and the pyrolysis vapor produced is swiftly transferred out of the pyrolysis reactor. In the high temperature range, these pyrolysis vapors have a shorter lifespan, which lowers the quantity of carbon deposition. Increasing the heating rate from 10 to 50 degrees Celsius, for example, reduced the biogas production by 3-8 percent (2013) ( D. Wang et al., 2020). As the heating rate rose from 10 to 50 ° C / min, the wood biogas output fell from 34.83 Wt to 31.95 Wt percent at the ultimate pyrolysis temperature of 400 °C. Increasing the heating rate from 5 to 40 °C/ min decreased the char performance from 38.8% to 26.4% wt. (D. Wang et al., 2020).

It is critical to prepare for the production of quick pyrolysis biochars. The biomass feed is heated to a temperature between 200 and 300 degrees Celsius, either directly or indirectly. Around 30% of the mass of the highly reactive chemical is transformed to combustible fumes during this process (Wang et al., 2017). Pyrolyzed biochar may develop, resulting in a lower potential for soil C sequestration due to higher carbon (C). Furthermore, employing a partly pyrolyzed biochar may cause microorganisms to immobilize soil nitrogen (Laird et al., 2009).

## 2.4 Biochar manufacturer's physicochemical properties

Only when the biomass and pyrolysis conditions are identical may two biochars be produced that are identical in terms of physico-chemical properties. Any slight modification in biomass, handling, or pyrolytic processing will result in an entirely different biochar. This necessitates a thorough examination of the different physical and chemical characteristics of the biochar generated.

### 2.4.1 Biochar’s chemical composition

During the pyrolysis of organic feedstock (biomass) used to produce biochemicals, biogas is broken down and the majority of its mass is lost in the form of volatile organic molecules. Experts believe that biogas restores the biomass's natural mineral and carbon structure (Aghoghovwia, Makhosazana P. 2018). Organic matter that has been pyrolyzed has much more carbon in it than organic matter that has not been pyrolyzed. Because of the changes in the biomass composition caused by pyrolysis, the recalcitrance of C in the biomass increases (Lehmann et al., 2009). Biochar may be a major source of plant nutrients once added to the soil since it is abundant in carbon, macro- and micronutrients. Specific processes and residency periods have been found by researchers. These include pyrolysis temperature and contact duration, which are particularly important for biochar specific surface area and recalcitrance, decomposers, and substrate, as well as organic matter interaction with mineral surfaces (D. Wang et al., 2020).

Soil organic carbon content increases as a result of changes in land management, a process known as soil carbon sequestration. Biochar has been shown to store carbon over a longer period of time. Consequently, soils treated with biochar store more carbon, helping to mitigate climate change. For soils to be effective in mitigating climate change, land management practices must result in an extra net transfer of carbon from the atmosphere to the soil, which varies depending on the soil and plant (Aghoghovwia, Makhosazana P. 2018; D. Wang et al., 2020).

The ration of labile carbon of biochemically utilized biogas to carbon dioxide. Its ‘compounds can occur in a variety of ways in biochemistry. Examples include microcrystalline carbon, carbon molecules, and organic molecules, to name a few. Mineral hydrocarbons can be found on the surface or inside the pores of biochar (Bhupinder Pal Singh & Annette L. Cowie., 2014). Organic compounds, which contain hydrogen and oxygen and are water soluble, are mineralized by soil organisms. Most permanent fraction of biochar is the amorphous or microcrystalline structure, which is mineralized on particle surfaces. This surface oxidation results in the formation of oxidized functional groups or clay complexes (Joseph et al., 2009).

Identification of black carbon by its labile percentage is believed to be essential for a variety of reasons. For example, using C accounting, it is possible to calculate the decomposition. Second, it permits the total soil matter accessible ratio to be determined as a source of C for bacteria (Thies and Rillig., 2009). The toxic metals have been discovered in some biochars, which may prevent plant germination or plant growth, Furthermore, because the labile fraction is frequently unstable, researchers can evaluate germination promotion and microorganism energy provision by determining its C composition (Girard; Flematti, 2004; and Steiner, 2008). The behavior of biochar, as well as its stability, is controlled by the pyrolysis conditions and the biomass parent material used in its production. The percentage of biogas that passes via short-term mineralization or biochemistry to carbon dioxide is known as the labile carbon fraction. Labile chemicals appear in a variety of ways in biochemistry. Microcrystalline carbon, carbon molecules, and organic molecules are only a few examples (Spokas., 2010). The Van Krevelen diagram is a graphic of the effect that compares the Oxygen/Carbon and Hydrogen/Carbon ratios of burnt materials depending on their elemental makeup to explain structural changes. Increased pyrolysis temperatures, for example, reduce the Hydrogen/Carbon and Oxygen/Carbon ratios, making biochars less susceptible to degradation (Spokas., 2010; Aghoghovwia, Makhosazana P. 2018). The Van Krevelen diagram is a graphical representation of this process that compares the Oxygen/Carbon and Hydrogen/Carbon ratios of charred materials (Aghoghovwia, Makhosazana P. 2018) depending on their elemental makeup in order to explain structural changes.

### 2.4.2 biochar surface chemistry

Processes and physicochemical features of biochar are frequently linked. When biochar is exposed to natural oxidation over time, an example of this can be seen Compared with fresh biochar or biochar incubated for one year, researchers (Aghoghovwia and Makhosazana P. 2018) discovered that the presence of biochar in soils for 130 years resulted in the formation of carboxylic and phenolic functional groups. The increase in oxygenated functional groups is attributed to changes in the elemental composition of biochar over time, with oxygen content increasing from 7.2 percent in fresh biochar to 24.8 percent in long-term oxidized biochar. The O/C of biochars with a half-life of 100-1000 years is 0.2-0.6, while biochars with a half-life of more than 1000 years is less than 0.20. Date palm biochars with a volatile matter concentration of less than 10% and an O/C ratio of 0.02-0.05 produced at pyrolysis temperatures of 500 °C are likely to have considerable C sequestration capacity, according to the findings (Usman Adel R. A. et al., 2015).

The pyrolysis temperature and the feedstock types have an impact on the surface area and pore size distribution of biochar. High-temperature biochar (600-700 degrees Celsius) produced biochars with a greater surface area than low-temperature biochar (400 degrees Celsius) (Aghoghovwia, Makhosazana P. 2018). (Biochars produced from plants (maize stover and aok wood) and manure-derived biochar (from chicken litter) generated at 600 degrees Celsius had more total surface area (527 and 642 $m^2$ $g^{-1}$, respectively) than the poultry liter biochar, which was generated at 400 degrees Celsius (94 $m^2$ $g^{-1}$). Comparing the total surface area of plant-derived biochars (maize stover, oak wood) and manure-derived biochars (chicken litter) generated at 600 degrees Celsius revealed that the plant-derived biochars (527 and 642 $m^2g^{-1}$, respectively) had a higher total surface area than the poultry litter biochar (94 $m^2$ $g^{-1}$). When applied to a soil containing a substantial amount of macropores, a high biochar surface area improves the retention of soil water as nutrients (Glaser et al., 2002).

### 2.4.3 Spectroscopic analysis of biochars

Amorphous structures and turbostratic crystallites are the classifications for ordered graphene layers, whereas amorphous structures and turbostratic crystallites are the classifications for disordered graphene layers. At pyrolysis temperatures below 600 °C, these disordered forms predominate, demonstrating biochar's great stability (Paris et al., 2005; Aghoghovwia, Makhosazana P. 2018). Fullerenes have hexagonal and pentagonal rings and are spherical formations (Harris., 2005). Fullerene-type structures are considered to contribute to biochar's high recalcitrance because of its folded shape.

O-aryl-C was formed when pine biochar was heated at pyrolysis temperatures less than 400 °C. Wood is mostly made up of cellulose (Baldock and Smernik., 2002). In burnt structures, Aryl C is the most prevalent C. The chemical changes involved with pyrolysis are commonly studied using aryl C as a starting point. It's been discovered that as heating temperatures rise, the amount of aryl C produced rises (Baldock and Smernik 2002).

## 2.5. Applications of biochars

The improvement of soil aeration and cation exchange capacity was lowered, and the soil structure and consistency were adjusted by altering the physical and chemical characteristics, according to the soil density and hardness of the solid. It also helps to restore damaged soils (Jyoti R. et al., 2019). Biochar's behavior and the factors that cause it have been studied through a number of studies using biochar alone and biochar integrated into the soil. The objective of this chapter is to provide a clear and precise analysis of relevant literature on biochar application, with a focus on nitrogen sorption and desorption behavior in biochar made from coffee grounds and woodchips, total soil organic (SOC) and total nitrogen (TN) characteristics of biochar applied to soil, and leachate and nitrogen release through biochar soil treated.

### 2.5.1. Adsorption and desorption of inorganic N

The current biochar sorption and desorption research attempts to determine if the nitrogen (N) in the biochar that was overlooked in earlier experiments is still present. A approach is to conduct a sorption and desorption experiment to determine the capacity of adsorption or absorption.

In a recent research, a maple wood biochar that had been pyrolyzed at 500 °C was used to assess the completeness of adsorption and to determine if nitrogen was removed from the biochar's surface during the experiment. The researchers took it a step further, testing the biochar for CEC and WHC content, as well as pH levels (Aghoghovwia, Makhosazana P. 2018). The pH of the biochar was left at its natural level (pH 8.7) in one batch, altered to pH 7 in another, and finally modified to pH values ranging from 3.7 to 8.1 in the final batch. At room temperature (16h extraction time), a batch adsorption test with 0.5 g biochar and 40 mL solution at concentrations ranging from 0 to 100 mg $NH_4^+$-N $L^{-1}$ was performed, and 15N labeling was utilized to determine if any ammoniums that were not recovered remained in the biochar. Water and a 1 M $NH_4Cl$ extraction were used to determine desorption. The ammonium adsorption was found to be unaffected when the biochar was left at its original pH level. However, the biochar modified to pH 7 exhibited a substantial increase in ammonium adsorption as oxidation increased. This occurred because when the pH was adjusted, the carboxyl and phenolic groups deprotonated and the free Aluminum (Al) and Fe precipitated, therefore forming the primary ammonium adsorption sites; moreover, this resulted in a reduced C content and a greater surface positive charge, resulting in a higher CEC (Brady and Weil., 2002; Aghoghovwia, Makhosazana P. 2018).

The residual adsorbed ammonium was nearly completely recovered by KCl at the low pH biochars after two extractions with ultrapure water. A high pH biochar was used to extract potassium chloride, which recovered 41-89 percent of the sorption of ammonium ($NH_4^+$-N) from the biochar. (Aghoghovwia, M. P., 2018). These investigations found that ammonium sorption in maple wood biochar is reversible and that the sorption mechanism is characterized by ion exchange. Furthermore, oxygen-containing functional groups and pH were discovered to have an impact on the adsorption capability of maple wood biochar.

Biochar ammonium adsorption has been studied using a range of feedstocks and pyrolytic temperatures. The research examined the ability of four type of biochar components (bamboo, Brazilian pepperwood, peanut hull, and sugarcane bagasse, as well as a hydrochar generated from peanut hull at 300 °C) created by slow pyrolysis at 350, 450, or 600 °C to remove inorganic nitrogen from solution (Aghoghovwia, M. P., 2018). The pH of biochar ranges from 5.2 to 9.1. Nine out of the thirteen biochars tested were shown to be capable of removing ammonium from solution. The clearance rates of biochar varied from 1.8 to 15.7 percent, with no discernible pyrolysis temperature trend ( Aghoghovwia, M. P., 2018).

According to (Hale et al., 2013), a batch sorption experiment was used to investigate biochar's ability to absorb ammonium fertilizer and release it on the surface as needed. In this work, coffee grounds and woodchips biochar were utilized as feedstocks for biochar formation, which was done at a temperature of 400 degrees Celsius for 2 hours. Biochars that had not been washed were compared to biochars that had been rinsed with Millipore water in the experiment. Biochars formed from cocoa shells and maize cobs, according to the research, can increase and slowly release ammonium into soil. Because $NH_4^+$ exchange allows biochars to absorb and release ammonium-nitrogen fertilizers via cation exchange, this result is crucial for agricultural production.

In the investigation, bamboo biochar generated at 900 degrees Celsius was shown to be 15% more efficient than activated carbons at eliminating nitrate from contaminated drinking water. Bamboo biochar was significantly more effective at absorbing nitrate than activated carbon, although having half the surface area (850 $m^2\ g^{-1}$). Another researcher found that the surface area did not match the anticipated sorbing potential and made a similar finding (Mizuta, 2004; Aghoghovwia, M. P., 2018).

New study has just proven the effectiveness of high-temperature biochar in eliminating nitrate. Even though the adsorption rate rose to 0.19 mg $NO_3^-$-N $g^{-1}$ biochar, the amount of nitrate adsorbed was decreased by 38% by weight at the maximum treatment level of 50 $mgL^{-1}$ (Aghoghovwia, Makhosazana P. 2018). According to (Yao et al., 2012; Aghoghovwia, Makhosazana P. 2018) to reports

Brazilian pepper wood, bamboo, peanut hull, and sugarcane bagasse biochars produced at 600 °C have been shown to have a high potential for nitrate adsorption. Biochars removed 0.12 to 3.7 percent by weight of the nitrate from the solution during a sorption experiment. They investigated the $NH_4^+$-N and $NO_3^-$-N sorption characteristics of sugarcane biochar produced at pyrolysis temperatures ranging from 400 to 800 °C (Kameyama et al., 2012; Aghoghovwia, M. P., 2018) utilizing sugarcane bagasse. According to the researchers, pyrolysis temperatures more than or equal to 700 °C resulted in significant $NO_3^-$-N adsorption when the temperature was greater than or equal to 700 °C. The biochars also have a high pH at high pyrolysis temperatures. (pH range: 8.7-9.8) Because the surface area and micropore volume of real nitrate adsorption were different, it was concluded that nitrate adsorption occurred as a result of base functional groups rather than physical adsorption.

Biochar includes tiny amounts of inorganic ($NO_3^-$-N), according to other tests, and it also eliminates $NO_3^-$-N from itself (Knowles et al., 2011; Jones et al., 2012; and Aghoghovwia, M. P., 2018). Biochars were produced at temperatures ranging from 600 to 900 degrees Celsius and retained nitrate sorption in tiny amounts on the surface. This indicates that pyrolysis temperature and biomass feedstock have an effect on biochar nitrate adsorption. Non-wood derived biochars adsorb more nitrate than wood-derived biochars generated at higher temperatures, according to the study (Kameyama et al., 2016).

### 2.5.2 Total soil organic carbon and total nitrogen

Biochar increases C/N ratio of a soil by increasing carbon availability, and it may result in increased immobilization concerning to the community of bacteria, fungal (Case et al., 2012; Liu., 2014). As a result, it's anticipated that soil nitrate immobilization caused by microbiological or physical processes following biochar application might assist minimize nitrous oxide emissions (Case et al., 2012).

The decomposed or breakdown of woods or debris by bacteria growth (or solubilize) on biochar surface and soil microorganisms have been speculated to be capable of degrading biochar (Hofrichter et al., 1999). The fungus Trichoderma has been shown to degrade biochar such as wood and boomboo biochar. Biochar has been used as the primary carbon source in a number of incubation studies to investigate the impact of microbial decomposition. Biochar breakdown by microbial transformations is currently poorly quantified. The extended times required to conduct these studies, according to (Kuzyakov et al., 2009), limit the ability to estimate the breakdown rate of biochar in order to ensure quantitative transformations.

### 2.5.3. Leaching of Inorganic Nitrogen (N)

Aside from looking into the effects of biochar's inorganic (mineral) N sorption capacity, the current study investigated the practical implications of applying N-retentive biochar to soil to minimize mineral N fertilizer leaching. The use of adsorption and desorption of $NO_3^-$-N experiments to analyze nitrogen and the decrease of nitrogen through leaching and release from itself to the environment, as this concept illustrates.

Biochar is well-known for having a high ion-holding ability. As a consequence of this information, (Yao et al., 2012) studied into the suitable adsorption and minimization of adsorbent cation - exchange biochars to mitigate ammonium and nitrate leakage from biochar-amended soils (Aghoghovwia, Makhosazana P. 2018). Biochar made from Brazilian pepperwood decreased $NH_4^+$ and $NO_3^-$ leaching, whereas peanut husk reduced nitrate and ammonium leaching by 14.4 and 34.3 percent, respectively (Yao et al., 2012). According to the study, bamboo biochar sorbed $NH_4^+$-N by CE and also low $NH_4^+$ -N leaching from 15.2% at a 20 cm depth, according to (Ding et al., 2010). Similarly, to (Kameyama et al., 2012; Aghoghovwia, Makhosazana P. 2018) reported that sugarcane biochar generated at 800°C showed highly effective $NO_3^-$ adsorption and reduced leaching by 5%. In a prior study, biochar reduced cumulative ammonium and nitrate leaching by 12 to 86 percent and 26 to 96% by weight, respectively (Sika and Hardie., 2014; Aghoghovwia, Makhosazana P. 2018).

Biochar made from Eucalyptus sp. (CEC 10 cmolc $kg^{-1}$) was conducted experiment with $(NH_4)_2SO_4$, added watered, and shaken for 504 hours. Biochar significantly decreased cumulative ammonium ($NH_4^+$) and nitrate ($NO_3^-$) leaching by 20% and 25%, respectively, when compared to the control without biochar treatment. Biochar's Eucalyptus sp. retentive characteristics were noticed in the experiment, and the comparatively low charcoal CEC was proposed as additional cause for the reduced leaching (Dempster et al., 2012; Aghoghovwia, Makhosazana P. 2018).

## 2.6. Knowledge gape

According to studies, biochar significantly reduced mineral fertilizer leaching (Sika and Hardie, 2014). On the other hand, the techniques and procedures behind it were unclear, as was the degree of its preservation. Their study focused on pine wood biochar and sugarcane application on sand loamy soil. In recent years, more biochar has been developed and used to crop growth. These new biochars' physiochemical properties have been identified. Furthermore, biochar made from coffee grounds and woodchips has not been fully explored. As a result, the objective of this research is to carry out a comprehensive physico-chemical evaluation of biochars on adsorption and desorption.

Application of biochar and mixed nitrogen as fertilizer, it is critical to understand how it interacts with nitrogen, as well as environmental concern. The potential biochar has on the sorption and desorption of ammonium and nitrate has an impact on mineral nitrogen release from old biochar, soils and crop area of study needs to be more thoroughly investigated. It is also uncertain how different biochar affects carbon and nitrogen mineralization in sandy soils. The phenomenon of the mechanism of biochar is also very important for this study to explore, especially it is the gap of knowledge for both coffee ground and woodchip biochars on soil amendment that will be improvement and development.

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# CHATPER 3

# PREDICTION OF THE POTENTIAL ADVANTAGES OF BIOCHAR WHEN SURPLUS NITROGEN FERTILIZERS IS APPLIED

## 3.1. Introduction

Nitrogen is a plant nutrient that is necessary for agricultural output to continue (Yan et al., 2014). The greatest source of nutrient fertilizer the soil is carbon and nitrogen included organic matter, which comes through breakdown of plant materials, microbes, and additional organic matter as nitrogenous compounds (e.g. manure in agricultural systems). The majority of nitrogen in agricultural systems is taken up by plants as ammonium ($NH_4^+$) or nitrate ($NO_3^-$). Ammonium is released through mineralization process while $NO_3^-$ is a product of nitrification process through $NH_4^+$ oxidation (Haygarth, 2005). This process was split into two parts: I $NH_4^+$ was converted to nitrite ($NO_2$) by ammonia-oxidizing bacteria, and (ii) $NO_2$ was converted to $NO_3^-$ by nitrite-oxidizing bacteria (Bernhard et al., 2010). Increased leaching of nitrate ($NO_3^-$) has made nitrogen losses from fertilizer techniques a major environmental problem across the world into water-bodies (Chen et al., 2015 and Zhou et al., 2019). Under tropical circumstances, N losses from fertilizer range from 20 to 30 percent (Cantarella et al., 2008), depending on N sources, soil moisture, and soil pH (Gallucci et al., 2018). Nutrient leaching is not only a problem of soil to function and plant uptake, but also can caused nutrient enrichment and eutrophication in water which affect human health. Human intake of excess $NO_3$, for example, could cause neonatal methemoglobinemia and a variety of malignancies.

As a result, removing excess inorganic N from soil solutions or waterbodies has significant ecological and socioeconomic consequences. To date, a variety of physical, chemical, and biological techniques for regulating inorganic N in the aqueous phase have been proposed, with biochar adsorption being one of the most popular (Hou et al., 2016).

Biochar is a plant-derived biomass produced by thermal degradation of organic materials through pyrolysis under conditions of limited oxygen (Ferddo et al., 2012 and Colin et al., 2012). Biochar is biodegradable and can serve as a home for symbiotic microorganisms due to its high total organic carbon content and suitable concentrations of micro- and macroelements (potassium, sodium, magnesium, calcium, copper, zinc, iron (Ding Y. et al., 2016), and others) (Tomezyk et al., 2020). Biochar is a porous material with a wide surface area, high sorption capacity, and cation exchange capacity that works as an environmental sorbent to reduce N and P leaching from soils (Cao, 2017; Lehmann and Joseph, 2003). Biochar's nutrient sorption ability varies depending on the kind of feedstock, the pyrolysis conditions (temperature, duration), and the soil types. The molecular structure and pore size distribution of biochar, which are variables that influence its sorptive behavior in the environment, have been shown to be altered by biomass types (feedstock) and high temperature during pyrolysis (Keiluweit et al., 2010). Biochar can be made from lignin-rich biomass, but it requires a high pyrolysis temperature (500 °C) to do so (Demirbas., 2006). Biochar, on the other hand, may have numerous unique characteristics at low temperatures, such as CEC, that promote nutrient absorption and crop output (Day et al., 2005). Heo et al., 2016 found that Giant reed biochar, pyrolysis at 500 °C, includes a lot of crystalline minerals with a lot of surface area, such KCl, $K_2O$, CaO, MgO, and SiO, enhances

$NH_4^+$–N adsorption in the solution pH values from 7 to 9. Furthermore, (Cao et al., 2016) revealed that the rice hull biochar application, pyrolysis at 500 ˚C for 30 min, not only enhanced concentration of $NH_4^+$ and $NO_3^-$, but also stimulate enzymatic and microbial activities in soil, and he finally concluded that soil types influenced on the response of $NH_4^+$ and $NO_3^-$ to biochar addition. Sorption and adsorption capacity of biochar can be measured through Freundlich or Langmuir coefficients models. At low water and biochar concentrations, $NH_4^+$ was adsorbed to rice hulk and a combination of tree trunks and branches derived-biochars, with Freundlich coefficients of 0.25 mg $g^{-1}$ in a previous research (Zhu et al., 2012 and Jones et al., 2012). Fourier transform infrared spectroscopy (FT-IR) and field emission scanning electron microscopy can be used to study the surface functional groups and micromorphology of biochars (Gai X. et al., 2014; FE-SEM).

Even though the sorption and release of inorganic N to and from biochar has been extensively studied, yet the effect of a combined woodchip and coffee-derived biochars on inorganic N adsorption and desorption at an optimum temperature and time were not underlined. Moreover, the adsorption and release kinetics of these biochars on inorganic N was not fully understood. In this chapter, the adsorption and desorption of coffee ground and woodchip biochars was conducted at lab scale to propose the mechanisms on soil manufacture and physiochemical properties. Due to research's purpose was to investigate into the adsorption and desorption capabilities of $NH_4^+$-N and $NO_3^-$-N on coffee and woodchip biochars that had been pyrolised at 400 °C for 2 hours, as well as the adsorption and desorption kinetics.

# 3.2. Materials and Methods

## 3.2.1. Biochar production

Coffee grounds and woodchips were used as raw materials for the production of biochar. The raw materials were collected from the coffee shop and as woodchip from the garden: Seoul National University (SNU). Before pyrolysis, the woodchips were chopped into small (2 cm) pieces and dried in an oven at 105°C for two days (48 hours). Under oxygen-limited conditions, the dry feedstock was transformed to biochar an automated biomass pyrolyzing furnace (TH-01, Germany). The pyrolysis temperature was increased to 400 °C, which was the target and held constant for 2 hrs. Heating rate was consequentially increased every 5 °C/min before reaching the constant temperature. After the pyrolysis process, biochar yields were recorded then It was ground to a fineness of 2 mm so that it could pass through a sieve.

## 3.2.2 Physiochemical properties of CBC, and WBC

Biochars was measured in 1:20 ratio of biochar to deionized water after shaking for 1h on a reciprocating shaker in room temperature at 25 °C. pH buffers ranging from 7 to 10 were used to calibrate the pH meter. The pH of the reference biochar was also measured in 0.01 M $CaCl_2$ with biochar to $CaCl_2$ ratio of 1:20 after shaking and equilibration for 1h, final pH was recorded by Orion star A216.

Ash, moisture, and volatile matter content of biochars and soil were performed based on ASTM standard method. The fixed carbon content was calculated by differentiation. The yield of biochars was calculated as follow:

$$\text{Yield (\%)} = [100 \times (\text{biochar mass} \div 105\ ^\circ\text{C dried biomass})] \qquad (1)$$

The mass loss that results is referred to as volatile matter (VM). The biochars were cooked at 550 °C for 6 hours in an open crucible. The amount of material left over after burning is referred to as ash content. The following equation was used to calculate the fixed carbon (FC) concentration:

$$FC\ (\%) = [\ 100 - (VM + Ash)] \qquad (2)$$

### 3.2.3 Physiochemical properties

After shaking for 1h on a reciprocating shaker with tube rotator in the room temperature at 25 °C. The measurement of soil pH was based on a 1:5 ratio of soil sample to deionized water. The calibrated meter pH adjusted with pH 7-10 buffers. After shaking and equilibration for 1h, we used in 0.01 M $CaCl_2$ solution for the pH measurement with 1:10 ratio, and the final pH was recorded by Orion star A216.

Dry combustion using a C, H, N, and S analyzer was used to determine the elemental compositions of biochars, which included C, H, N, and S. elemental analysis (EA). Briefly, 1.0 g of ground samples were introduced into a high temperature (1,000 °C) furnace and combusted in pure oxygen under static circumstances. Combustion converts carbon to carbon dioxide, hydrogen to water, nitrogen to nitrogen gas/oxygen oxides, and sulphur to sulphur dioxide (Akoji Jibrin N. et at., 2019). After passing through the absorption traps, only carbon dioxide, water, nitrogen and sulphur dioxide remained, which were then detected and recorded. Each element's weight percentage was determined.

$$O\ (\%) = [\ 100 - (C + H + N + S + ash)] \qquad (3)$$

The atomic ratios of biochar, including H/C, O/C and (O+N)/C, were calculated according to (Chen B. et al., 2008).

### 3.2.4. Extractable cations of CBC400, WBC400, and Soils

The composition of major elements, including $Ca^{2+}$, $Mg^{2+}$, $Na^{+}$, and $K^{+}$ in coffee grounds and wood crisps was determined by microwave-assisted acid digestion and optimal emission spectrometry with inductively coupled plasma (ICP-OES, Optima 8000, PerkinElmer). Briefly, 5.0 g of biochars and soil samples were extracted with 60 mL of 1 mol $NH_4$-acetate (pH 7) in 100 mL syringe containing 0.5g of N-free pulp, then the samples were displaced for 8h. Samples were then displaced with 60 mL of isopropyl alcohol prior to extract with 60 mL of 10 % NaCl.

### 3.2.5. FTIR and BET (Brunauer-Emmett-Teller method)

The biochar samples were ground to a powder and FTIR spectra were recorded using an FTIR spectrometer (Perkin Elmer Frontier) with a spectral range of 4000 - 600 $cm^{-1}$ over an average of 64 scans. The FTIR spectra were interpreted using the broadband chemical group assignments given in (Jindo et al., 2014).

### 3.2.6. Adsorption and desorption of $NH_4^+$–N and $NO_3^-$–N

#### 3.2.6.1. Adsorption isotherm

The stock solution was prepared with 1,000 mL of $NH_4^+$-N and $NO_3^-$-N after $NH_4Cl$ and $KNO_3$ were dissolved in deionized water to 1,000 mg $L^{-1}$. The experiment was carried out at a temperature of 25 °C. Adsorption studies were performed in 50 mL conical tubes containing 20 mL of dilute $NH_4^+$-N and $NO_3^-$-N solution (Park M.H. et al., 2019). Adsorption capacity (Park M.H. et al., 2019) of controlled coffee ground and woodchip was used in a 50 mg $L^{-1}$ $NH_4^+$-N and $NO_3^-$-N (Xiapu Gai1 et al., 2014) solution with a 0.5 g $L^{-1}$ dose of biochar and soil samples. Initial concentrations of $NH_4^+$-N (10, 20, 30, 40, 50, 100, 200, 300, 500, and 600 mg $L^{-1}$

$NH_4^+$-N), and $NO_3^-$-N (0.5, 5, 10, 15, 20, 25, and 30 mg $L^{-1}$ of $NO_3^-$-N) 1.0 M Na Acetate was used to modify the pH of the solution for the pH effect investigation. To validate the presence of $NH_4^+$ (aq) and $NO_3^-$ in the solution, the final pH (starting pH = 7.0) was measured (aq). A tube rotator was used to spin the test tubes at 60 rpm during the testing. For the batch trials, the contact period was 72 hours to guarantee adsorption equilibrium. The following equation was used to calculate the adsorption equilibrium time:

$$q_e = \frac{(C_0 - c_e).V}{M} \tag{4}$$

where $q_e$ is the equilibrium adsorption capacity (Park M.H. et al., 2019) of biochar in mg $g^{-1}$, $C_0$ is the initial $NH_4^+$-N and $NO_3^-$-N concentration in mg $L^{-1}$, and $C_e$ is the equilibrium $NH_4^+$-N and $NO_3^-$-N concentration in mg $L^{-1}$. M is the dry mass of the biochar in grams, and V is the volume of $NH_4^+$-N and $NO_3^-$-N solution in one liter. Each of aforementioned adsorption experiments repeated three times. The efficiency of removal was calculated using the equation of $NH_4^+$-N and $NO_3^-$-N as below:

$$R_e = \frac{(C_0 - C_e).100}{C_0} \tag{5}$$

where $R_e$ denotes the $NH_4^+$-N removal efficiency in percent and $NO_3^-$-N denotes the NO3-N removal efficiency in percent.

### 3.2.7. Adsorption and desorption kinetics of $NH_4^+$N and $NO_3^-$-N

#### 3.2.7.1. The Kinetics of Adsorption

The kinetics of $NH_4^+$-N and $NO_3^-$-N adsorption on coffee grounds and woodchip biochars were investigated in batch adsorption experiments under isothermal conditions. In all, 100 mL of $NH_4Cl$ and $KNO_3$ solution were produced in a 100 mL conical glass flask and shaken for up to 120 minutes at 25 °C on a rotatory shaker at 60 rpm. The suspension (0.1 mL) were collected at 5, 15, 30, 60, 75, 90, 105. And 120 minutes. The solid mass loss was minimal throughout sampling time because the solids in the suspensions were rapidly separated from the liquid phase. The solutions were tested for $NH_4^+$-N and $NO_3^-$-N (Rahil, M.H et al., 2007) by ultra-spectrophotometer after passing through a 0.45 mm Millipore filter. An ultraviolet wave spectrometer (HS -3300, HUMAS Co., Ltd, Republic of Korea) was used to measure the amounts of $NH_4^+$-N and $NO_3^-$-N (Paramasivam S. et al., 2000; Park M. H et al., 2019). Nessler technique and chromatropic acid method were used with minor modifications to determine the concentrations of $NH_4^+$-N and $NO_3^-$-N in the samples (Park M. H et al., 2019). Both $NH_4^+$-N and $NO_3^-$-N had an initial concentration of 50 ml $L^{-1}$. Samples of 0.5 g biochar were added to the solution (Park M. H et al., 2019) and manually panned at a room temperature of 25 °C using a tube rotator at 60 rpm. The concentration of an aliquot (0.5 mL) of the solution was checked regularly (Park M. H et al., 2019). $NH_4^+$-N and $NO_3^-$-N concentrations. The following formulas were used to determine the concentrations of $NH_4^+$-N and $NO_3^-$-N:

$$q_t = \frac{(C_0 - C_t).\mathrm{V}}{\mathrm{M}} \qquad (6)$$

where $q_t$ is the mass of $NH_4^+$-N and $NO_3^-$-N adsorbed and desorbed per unit mass of biochar in mg $g^{-1}$ at time *t* (Gai X. et al., 2014).

### 3.2.7.2 Desorption kinetics

After the adsorption experiment, the residual solution in the tubes was decanted, and 50 mL of distilled water was added as stated for the adsorption experiment above. This process was repeated 10 times every three days, yielding two stages of desorption. The continuous flow analyzer was used to measure ammonium N concentrations in the supernatant within 24 hours.

### 3.2.7.3 Extraction and Repetitive $NH_4^+$-N and $NO_3^-$-N

After the releasing kinetics experiment, the biochar samples were filtered out of the deionized water and fresh water was added every three days to release nitrogen (N). The kinetics and release tests were carried out three times, with the average results and standard deviation and variance provided.

### 3.2.8. Analytical methods

The average of three replications was used to determine the outcomes of the adsorption and desorption studies. The following equations was analyzed to fit data adsorption to both Freundlich and Langmuir isotherm models:

Langmuir isotherm:

$$q_e = \frac{q_{max}\ bCe}{1+bCe} \tag{7}$$

where $q_e$ is the equilibrium adsorption capacity of the adsorbent in mg $g^{-1}$, $C_e$ is the equilibrium concentration of the adsorbate in mg $L^{-1}$, $q_{max}$ is the maximum adsorption capacity of the metal at energy in mg $g^{-1}$, and b is the Langmuir constant with respect to the energy of the adsorption capacity at equilibrium in mg $g^{-1}$ (L $mg^{-1}$).

Freundlich isotherm:

$$q_e = K_f C_e^{1/n} \tag{8}$$

where $K_f$ is the Freudlich constant relating to the adsorption capacity of the adsorbent, and $n$ is the empirical constant relating to the adsorption intensity as a function of the type of sorption site.

Adsorption and desorption kinetics models:

1) Equation of Pseudo- first-order rate equation:

$$q_t = q_e(1 - \exp(-k1t)) \quad (9)$$

Where $q_t$ is the adsorbed mass of $NH_4^+$-N and $NO_3^-$-N per unit mass of the samples at time t in mg $g^{-1}$, $q_e$ is the adsorption capacity of the adsorbent at equilibrium in mg $g^{-1}$, and $k_1$ is the first-order pseudo-rate constant in mg $g^{-1}$ $min^{-1}$ (Park M. H. et al., 2019).

2) Pseudo- second- order rate equation**:**

$$q_t = \frac{k_2 q_e \ 2t}{(1+1+k_2 q_e t)} \quad (10)$$

where $k_2$: Pseudo-second-order rate constant in (g $mg^{-1}$)

3) Elovich equation:

$$\frac{dq_t}{d_t} = aexp(-\alpha qt) \quad (11)$$

where a is the Elovich constant proportional to the initial adsorption rate in (mg $g^{-1}$ $h^{-1}$), and α is the Elovich constant proportional to desorption (mg $g^{-1}$ $h^{-1}$).

## 3.3. Results and Discussion

### 3.3.1. Physiochemical Characteristics of Biochars from CBC, and WBC

As shown in Table 3. 1, we have observed general dependent pH of the initial CBC and WBC. WBC400 and CBC400 had pH ranged from moderately alkaline (pH 8.47) to alkaline (pH 9.32), respectively. CBC400 had higher pH than WBC400 and the difference pH between both biochars were about 1. The high concentration of inorganic soluble salts matches the biocahr's basic pH. These findings corroborate prior research that found biochars to be alkaline (Singh., 2010). Alkaline biochar has a liming effect when used to amend acidic soil. While biochars are applied to moderately acidic soils, a number of problems arise. For example, a soil pH of more than 8 may have an adverse effect on plant growth and may deplete available P as well as several micronutrients (Artiola et al., 2012). Proton activity was minimal in the alkaline biochar, indicating that the displacement of protons from hydration solutions was favored, because biochar surface almost negative electron (Essington et al., 2004). Under pyrolysis temperatures and time, both biochars produced similar yields which varied from about 32.49% for CBC and 33.93% for WBC (Table 1). The black C proportion in biochars is represented by the fixed C content, which is used to calculate biochars' soil lifetime. The non-combustible mineral fraction of biochars is referred to by the percentage of ash, whereas the non-combustible mineral fraction of biochars is referred to by the percentage of ash. The percentage of ash content in CBC (2.9%) was lower than ash content in WBC (11.6%), however, its ash contents were greater than coffee residue (CR) 0.73% and 1.7% (Tsai et al., 2012; Naruephat T., 2019). Many studies have shown that biochars with a high ash content are nutritious and alkalizing (Deenik JL et al., 2011). Although CBC had low ash, it was high fixed C (81.25%) as compared to WBC (67.63%) and both of which had fixed C above 50% and low volatiles matters, indicating good potential for carbon sequestration.

Biochars in this study had high C and low N which brought about high C/N ratio, ranging from about 52 for CBC and 312 for WCB, respectively. When added biochars to soil, a carbon and nitrogen fraction > 30:1 has negative repercussions and can result in net nitrogen immobilization (Havlin et al., 2014). Both biochars studied might possibly lower mineral N as a result of the nitrogen (N) immobilization process.

In terms of CBC and WBC H/C and O/C ratios, they ranged from 0.17 to 0.61 percent and 0.59 percent to 0.86 percent, respectively in Table 2. The H/C ratio should have a maximum threshold value of 0.7, according to (IBI., 2015), while the O/C ratio should have a maximum threshold value of 0.4, according to EBC 2012. When the atomic ratios of biochars are higher, they exhibit less carbonization, aromaticity (H/C), and polarity (O/C). The O/C and H/C ratios in the biochars of this study were close to the prescribed limits, indicating that the biochars had low oxygen content and high C content and were therefore categorized as well-pyrolyzed areas with aromatic structure enrichment, degradability, and stable properties (Masiello 2004). The O/C and H/C ratios in WBC were lower than in CBC. This suggested that WBC enriches higher aromatic structures and more stable while CBC has higher chemical reactivity and less hydrophilic surface. However, both biochars exhibited similar water holding capacity which was around 27.4%.

The specific surface area, pore volume, and pore size of CBC and WBC are summarized in Table 3.1. (Gai Xiapu et at 2014). The surface area of biochars is a measure of how well its surface form adsorbs different solutes (Lehmann et al., 2006). Biochar pore structures revealed the structural changes in biochar particles following thermal treatment, and the pore diameters or sizes of the structure

**Table 3.1.** Physicochemical properties of coffee ground (CBC) and Woodchip (WBC) biochars pyrolyzed at 400 °C for 2 h.

| Characteristics | | Biochar | | Aromaticity criteria |
|---|---|---|---|---|
| | | Coffee ground | Woodchip | |
| Yield (%) | | 32.49 | 33.93 | |
| pH | | 9.32 | 9.83 | |
| Proximate analysis (wt.%, dry-basis) | Fixed carbon | 81.25 | 67.63 | |
| | Volatile matter | 15.85 | 20.77 | |
| | Ash | 2.9 | 11.60 | |
| Ultimate analysis (wt.%, dry basis) | C | 52.45 | 78.0 | |
| | H | 3.7 | 3.84 | |
| | N | 1.0 | 0.25 | |
| | O | 42.85 | 17.91 | |
| | H to C | 0.85 | 0.59 | < 0.6 |
| | O to C | 0.61 | 0.17 | < 1.7 |
| Elemental composition (g/kg) | K | 19.16 | 4.82 | |
| | Ca | 1.74 | 7.87 | |
| | Mg | 1.04 | 1.06 | |
| | Na | 1.15 | 8.86 | |
| Surface area ($m^2$ $g^{-1}$) | | 0.44 | 2.91 | |
| Pore volume ($cm^3$ $g^{-1}$) | | 0.011 | 0.011 | |
| Mean pore diameter (nm) | | 98.28 | 14.92 | |
| CEC (cmol $kg^{-1}$) | | 29.67 | 31.44 | |
| WHC (% by wet wt.) | | 27.4 ± 4.9 | 27.4 ± 4.9 | |

were a critical attribute for becoming sorbent materials. WBC had higher surface area (2.91 $m^2$ $g^{-1}$) than CBC (0.44 $m^2$ $g^{-1}$), indicating that WBC might be good for nutrient adsorption than CBC, however, both of which had low surface area. The low surface area might relate to the pyrolytic temperature (Joseph et al., 2009) and the processes of softening, melting, fusion, and carbonization during pyrolysis (Fu et al., 2011). These processes restrict gas adsorption from entering the pores, resulting in reduced surface areas. The inclusion of compositional components (lignin, cellulose, and hemicellulose) in feedstock contributes to WBC's large surface area (Kizito et al., 2019). CBC and WBC had similar pore volume, but different in mean pore diameters. CBC (98.98 mn) had higher mean pore diameter than WBC (14.92 mn).

CEC is a significant source of biochars and soil that contributes in nutrient adsorption and desorption, as well as nutrient retention (Glaser et al., 2001). CEC estimations for biochar vary widely, ranging from 5 to 50 cmol $kg^{-1}$ in some situations and up to 69 to 204 cmol kg1 in others (Echeverri et al., 2018). A study comparing maize stover biochar pyrolyzed at 450 °C and 700 °C found that the lower temperature yielded biochar with twice the CEC value as the high pyrolysis temperature (Aghoghovwia, Makhosazana P., 2018), indicating that adding lower pyrolytic biochar to soil can increase soil CEC and contribute to C sequestration (Aghoghovwia, Makhosazana P., 2018). The CEC value of the biochar was similar and averaged between 29.67 and 31.44 cmol $kg^{-1}$. The CEC value of the topsoil was in the average range, indicating that it is capable of retaining and exchanging cations in the soil solution.

### 3.3.2. Soil's physiochemical characteristics

As indicated in Table 3, the physiochemical characteristics of the original soil sample were investigated. The pH of the soil sample was 6.55 on average. The pH range used in this investigation was suitable for vegetables. Most plants can tolerate a soil pH of 6.0 to 7.5 because most nutrients are available in this range (FAO, 2021). Plants can grow in soils with bulk density of 1.38 g $m^3$. The CEC was used together with the mean concentrations of carbon (20.7 g $kg^{-1}$) and nitrogen (1.5 g $kg^{-1}$) (Chen X. Y. et al., 2007). The initial soil's C/N ratio was also normal, and it was comparable to that of other cultivated soils. The water filter pore space and water retention capacity were both within acceptable limits.

**Table 3. 2.** Physicochemical properties of the initial soil collected at SNU loop top of plot experiment.

| **Characteristics** | **Soil (initial soil)** |
|---|---|
| Bulk density (g cm$^3$) | 1.38 |
| pH (1:5) | 6.55 |
| Total soil organic carbon (g kg$^{-1}$) | 51.32 |
| Total nitrogen (g kg$^{-1}$) | 3.69 |
| Pore volume (cm$^3$ g$^{-1}$) | 0.21 |
| C/N ratio | 13.82 |
| CEC (cmol$_c$ kg$^{-1}$) | 14.25 |
| Water holding capacity (% by wet. Wt.) | 48.02 |
| Water filter pore space (%) | 43.59 |

### 3.3.3 Extractable cations of CBC, WBC, and Initial Soils

The biochars and soil varied quite widely in their initial extractable cations as shown in Figure.3.2. The overall ranges of extractable cations for biochars and initial soil samples ranged from 0.2 to 10 mg/g, respectively. The initial soils had higher extractable Ca than Mg, K, and Na. The extractable K in CBC were extremely higher than Na, Ca, and Mg, in contrast, the extractable Ca and Na in WBC were similar and higher than K and Mg. Since the pyrolysis temperature and time were similar for both biochars, the large differences in extractable cations were more likely related to the precursor feedstock. In this study, the main element in CBC, WBC, and the initial soil were exchangeable K, Na, and Ca, respectively.

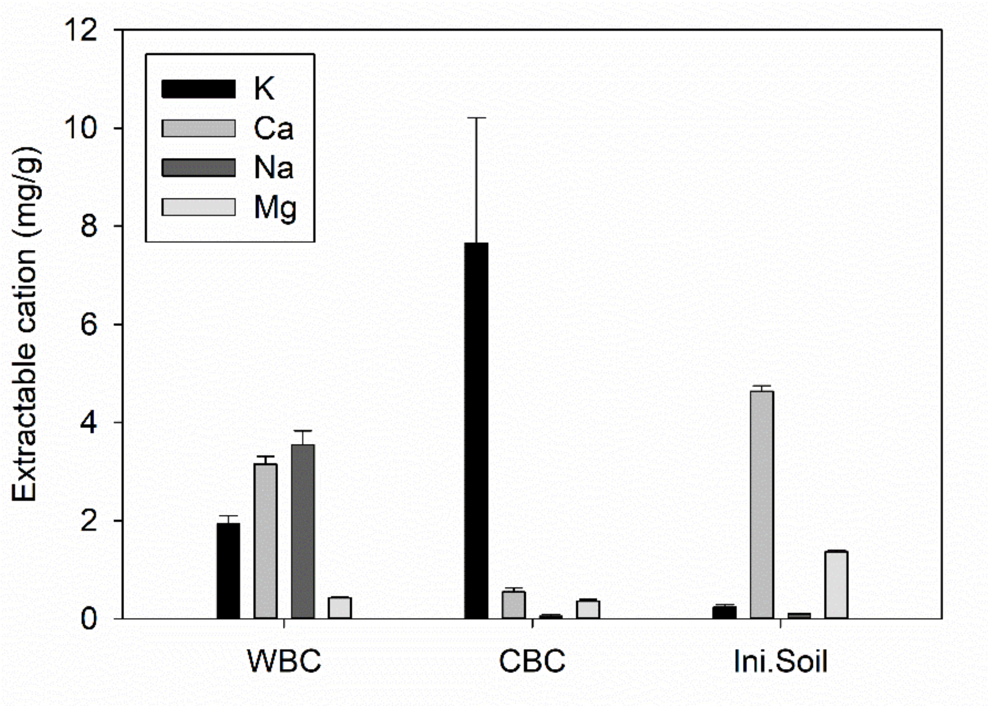


**Figure. 3. 2.** Exchangeable cations of the initial soil, CBC, and WCB.

### 3.3.4. Electrical conductivity of soil salinity

Salinity is one of the most serious environmental variables limiting crop yields, as most crops are susceptible to salinization due to excessive salt concentrations in the soil, and the area affected by it is increasing daily. Drought and excessive soil salinity are the main causes of salinity loss, which will exacerbate in many places as a result of global climate change.

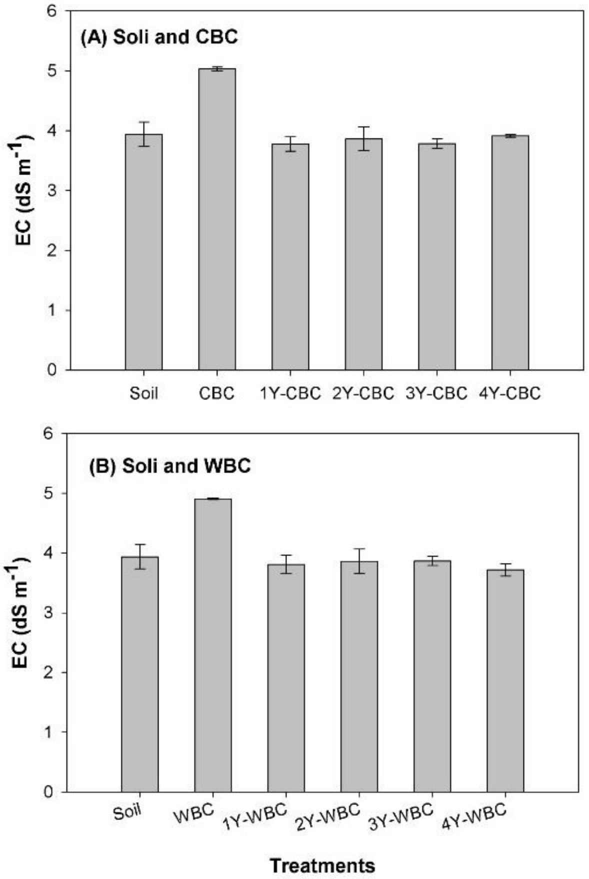


Figure. 3. 3. The impact of biochars and soils on electrical conductivity (EC) before and after Pak Choi harvested; (A) soil plus CBC, and (B) soil mixed with WBC.

In comparison to the control, the EC was evaluated among both the highest and lowest application rates. The EC was high enough to outperform the EC of the control, which had a higher biochar concentration. The EC increased (although not dramatically) with 5.0 % biochar before planting, and it increased similarly after planting.

As a result, for all treatments, increasing the biochar dosage over time in the soil had no effect on the EC. Its average crop productivity yield (20% to 50% of record yields) ranges from 20% to 50%. (Shrivastava P. and Kumar R., 2014).

## 3.3.5. FTIR and Scanning Electron Image (SEM) Analysis and BET (Brunauer-Emmett-Teller method)

### 3.3.5.1 FTIR –Analysis

The FTIR spectra of the two biochars, CBC and WBC, pyrolysed at 400 ˚C for 2 h were shown in Figure 2. Biochar is a kind of carbon polymer containing various functional groups on the surfaces due to different preparation conditions (Gai X. et al., 2014). Hydroxyl (OH), aliphatic alkyl (CH2), aromatic C=C, and COOH functional groups were assigned to the peaks in the spectra. The variations in the spectrum were due to changes in the surface functional groups of biochars. The –OH band intensity of CBC and WBC decreased dramatically at ~3400 cm$^{-1}$ while –$CH_2$ band intensity of CBC was slightly decreased and WBC was almost preserved at ~2900 cm$^{-1}$, respectively. Carbon condensation caused the strong peaks of C=C and COOH to drop at 1350 cm$^{-1}$ and 1600 cm$^{-1}$ for both CBC and WBC (Zhao et al., 2013).

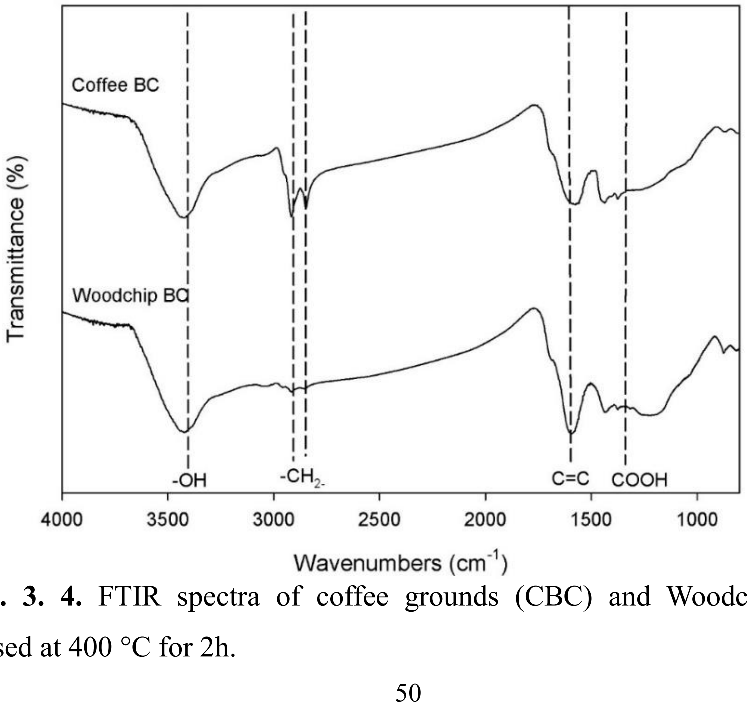


**Figure. 3. 4.** FTIR spectra of coffee grounds (CBC) and Woodchips (WBC) pyrolysed at 400 °C for 2h.

### 3.3.5.2 Surface Area and Pore Volume of Biochars

The specific surface area of biochar BET reflects how well it adsorbs various solutes on its surface form (Table 3.3). When compared to CBC400, WBC400 had a larger BET surface area. Feedstocks and pyrolyzed temperature may be causing variations in BET surface area between WBC400 and CBC400. According to (Shohi et al., 2010), different feedstocks lead to different surface area sizes, pores and functional groups in biochar, and all these parameters affect the sorption properties of biochar (Gai X. et al., 2014). The low specific surface area BET of CBC400 and WBC400 biochar could be due to the high content of inorganic alkaline species, which may limit the surface area by preventing access to the micropores of the biochar (Aghoghovwia, Makhosazana P., 2018).

**Table 3. 3** Surface area and pore volumes of CBC and WBC pyrolysed at 400 °C for 2h.

| **Sample** | **BET Surface Area** | **Micropore Volume** | **Total Pore Volume** | **Average Pore Diameter** |
|---|---|---|---|---|
| | ($m^2$ $g^{-1}$) | ($cm^3$. $g^{-1}$) | ($cm^3$. $g^{-1}$) | (nm) |
| CBC400 | 0.4378 | 0.1006 | 0.1076 | 98.2810 |
| WBC400 | 2.9061 | 0.6677 | 0.1084 | 14.9240 |

### 3.3.5.3 Scanning Electron Image (SEM) analysis

When biochar structure is blocked, surface area, pore volume, and pore diameter change (Zewen Jin et al., 2016). The exposure of WBC (c) and (d) had more interior surfaces structure than CBC (a) and (b). CBC has much rougher surface area and show signs of collapse. Since carbonization of biomass material takes a long time, pore structure is a crucial factor in determining adsorption capacity (Zhongxin Tan et al., 2017). Therefore, WBC has more chance to enhance exposure of inorganic minerals as it increased in the pore structure comparing to CBC.

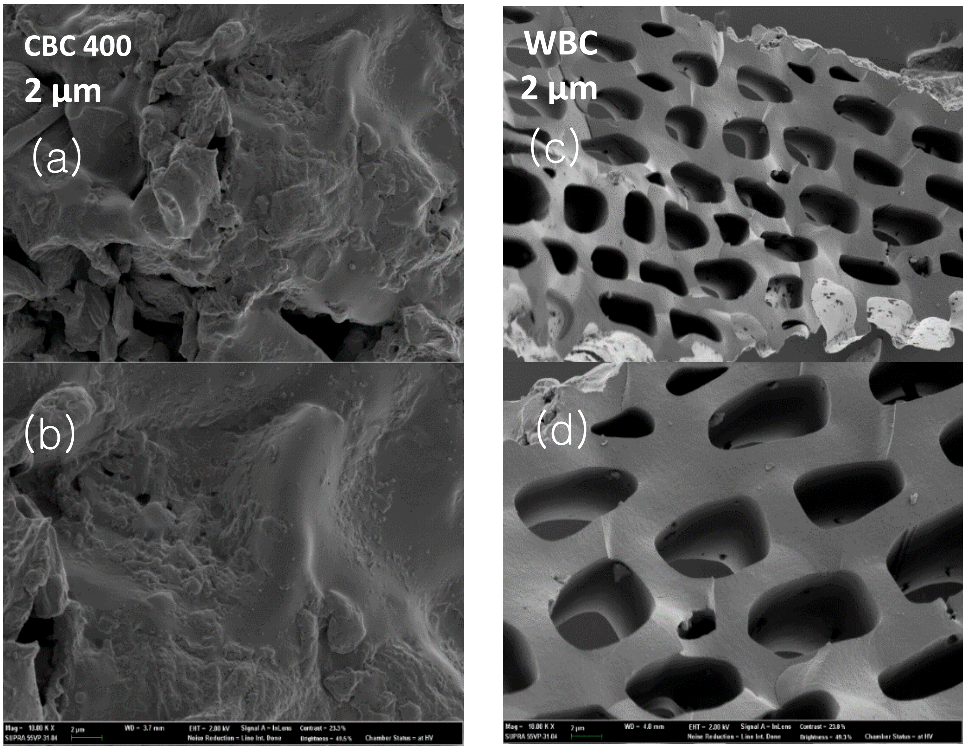


**Figure. 3.5** Scanning electron microscopy (SEM) images for the surface morphology of CBC and WBC at 400 ˚C for 2 hr. (a) CBC 2 μm, magnification 5.00 k and (b) 10.00 k. (c) WBC 2 μm size image 5.00 k and (d) 10.00 k.

### 3.3.6 Adsorption and desorption $NH_4$-N and $NO_3$-N on CBC, WBC and soils surface

#### 3.3.6.1 Adsorption isotherm of $NH_4^+$-N and $NO_3^-$-N

As Table 3.4. shows the Langmuir and Freundlich isotherm constants adsorption (Purkait M. K. et al., 2005), and desorption capacity of biochars on $NH_4^+$ and $NO_3^-$. Models of the adsorption data yielded correlation coefficient $R^2$ values over 0.8837. Langmuir model showed higher linear fitting ($r^2 = 0.9998$) as compared with WBC ($r^2 = 0.9769$). This indicate that Langmuir is better than Freundlich model. The adsorption process was presented by Langmuir model very well, and correlation coefficient ($R^2$) values were all higher than 0.9469. Values $q_{max}$ in the Langmuir model were higher than 3.373, suggesting that the adsorption process is favorable. This indicate that is the good adsorption performance of $NH_4^+$-N on biochar. In terms of binding energy, it is generally assumed that a homogeneous adsorption surface contains only one type of adsorption site (Kumar Vasanth, K., 2019).

**Table 3. 4.** Parameters of Langmuir, and Freundlich adsorption isotherm of $NH_4^+$-N onto CBC and WBC surface

| **Sample** | **Langmuir isotherm** | | | **Freundlich isotherm** | | |
|---|---|---|---|---|---|---|
| | $q_{max}$ (mg/g) | b (L/mg) | $R^2$ | $K_f$ (mg/g) ( L/g)$^n$ | n | $R^2$ |
| CBC400 ($NH_4^+$-N) | 4.9848 | 0.0028 | 0.982 | 0.0555 | 1.563 | 0.974 |
| WBC400 ($NH_4^+$-N) | 9.285 | 0.0237 | 0.977 | 1.576 | 3.535 | 0.884 |
| CBC400 ($NO_3^-$-N) | 3.373 | 0.0225 | 0.999 | 0.319 | 2.449 | 0.972 |
| WBC400 ($NO_3^-$-N) | 3.810 | 0.0233 | 0.9998 | 2.515 | 2.533 | 0.966 |

We were able to calculate the adsorption capacity of CBC and WBC on $NH_4^+$-N and $NO_3^-$-N using Langmuir and Freundlich adsorption isotherms (Figure. 3.4). The results showed that the adsorption data on CBC 400 was well fitted with both of Langmuir ($R^2 = 0.9469$) and Freundlich ($R^2 = 0.9454$) in compared with other adsorbents (Van T. N et al., 2019). Thus, CBC showed a good adsorption performance. The Langmuir demonstrated that increasing the number of active sites on the composites for aqueous $NH_4^+$-N adsorption enhanced the capacity of WBC in (Figure.3.4b) (Kumar Vikrant et al., 2018). The carbon has a large surface area and exchangeable interlayer ions that can be exploited as active sites for adsorption by anion exchange and surface complexation (Kumar Vikrant et al., 2018). Therefore, the mechanism of this increased has been discussed adsorption process for $NH_4^+$-N was favorable in this experiment. Suggesting a high potential material in the future (Zhou et al., 2017).

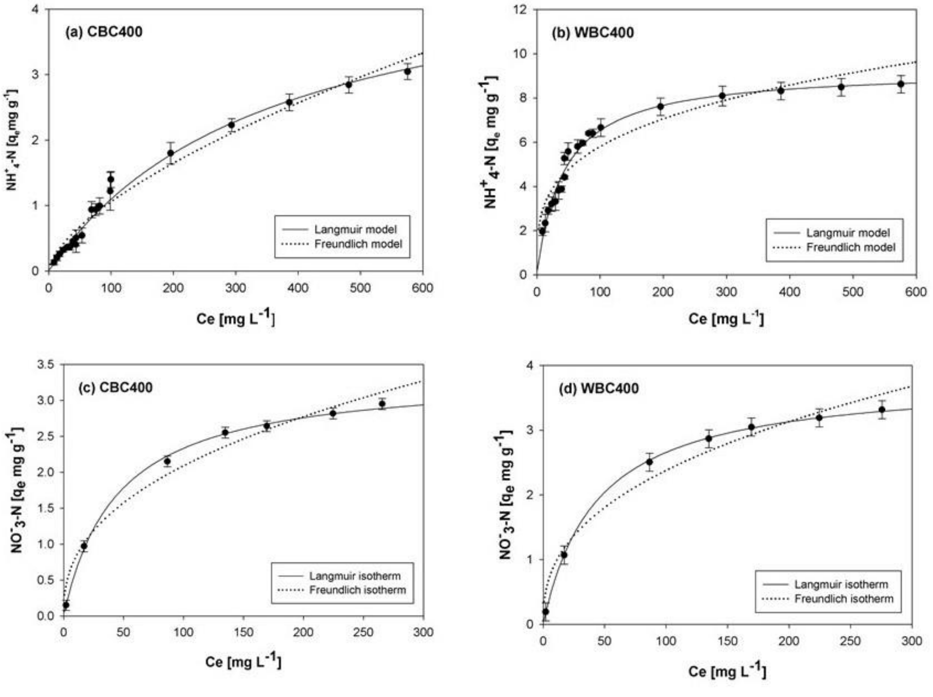
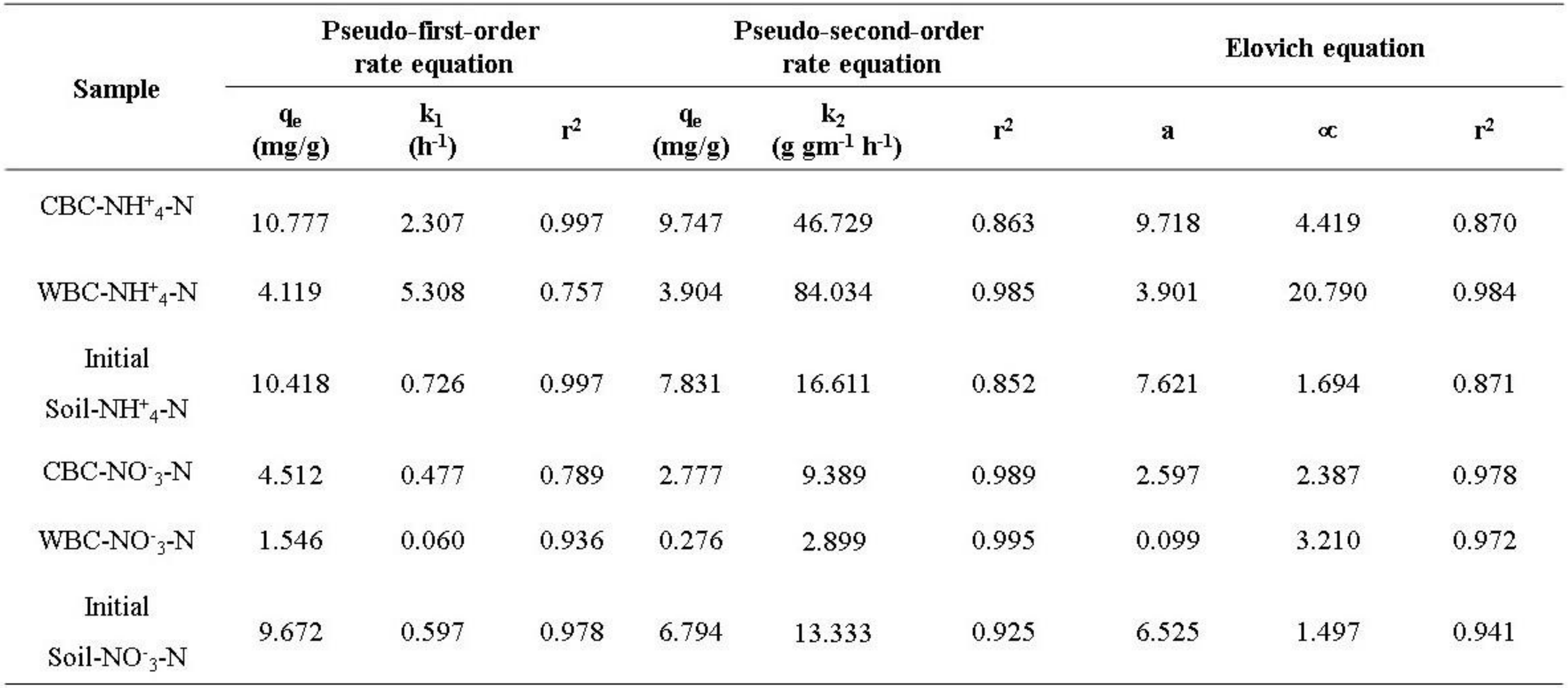


**Figure.3.6** Adsorption isotherms of $NH_4^+$-N (a) (b) and $NO_3^-$-N (c) (d) onto CBC and WBC surfaces using Langmuir and Freundlich methods.

### 3.3.6.2 Adsorption kinetics of $NH_4^+$-N and $NO_3^-$-N onto CBC, WBC and initial Soils

We investigated the adsorption kinetics of both biochars and starting soils on $NH_4^+$-N and $NO_3^-$-N, as shown in (Table. 3.4), and (Figures 3. 5a), (3. 5b), (3. 5c), (3. 5d), (3. 5e), and (3. 5f). The result showed that both biochars had better fitted to different fitting models. $NH_4^+$ (Figure. 3.5e) and $NO_3^-$ (Figure. 3.5f) of the initial soil were fitted well with Pseudo-first-order. $NH_4^+$ of CBC and WBC were also fitted well with Pseudo-first-order. In contrast, $NO_3^-$ of CBC and WBC fitted well with

**Table 3. 5** Adsorption kinetics model parameters for $NH_4^+$-N and $NO_3^-$-N adsorption onto CBC, WBC, and initial soils.



| Sample | Pseudo-first-order rate equation | | | Pseudo-second-order rate equation | | | Elovich equation | | |
|---|---|---|---|---|---|---|---|---|---|
| | $q_e$ (mg/g) | $k_1$ ($h^{-1}$) | $r^2$ | $q_e$ (mg/g) | $k_2$ (g $gm^{-1}$ $h^{-1}$) | $r^2$ | a | ∝ | $r^2$ |
| CBC-$NH^+_4$-N | 10.777 | 2.307 | 0.997 | 9.747 | 46.729 | 0.863 | 9.718 | 4.419 | 0.870 |
| WBC-$NH^+_4$-N | 4.119 | 5.308 | 0.757 | 3.904 | 84.034 | 0.985 | 3.901 | 20.790 | 0.984 |
| Initial Soil-$NH^+_4$-N | 10.418 | 0.726 | 0.997 | 7.831 | 16.611 | 0.852 | 7.621 | 1.694 | 0.871 |
| CBC-$NO^-_3$-N | 4.512 | 0.477 | 0.789 | 2.777 | 9.389 | 0.989 | 2.597 | 2.387 | 0.978 |
| WBC-$NO^-_3$-N | 1.546 | 0.060 | 0.936 | 0.276 | 2.899 | 0.995 | 0.099 | 3.210 | 0.972 |
| Initial Soil-$NO^-_3$-N | 9.672 | 0.597 | 0.978 | 6.794 | 13.333 | 0.925 | 6.525 | 1.497 | 0.941 |

Pseudo-second-order. It is obvious that $NH_4^+$-N and $NO_3^-$-N adsorption is quick at first and later slows down. Maximum adsorption was reached in 120 min. The two biochars sorbed the ammonium ($NH_4^+$ -N) and nitrate ($NO_3^-$-N) in aqueous solutions in relatively fast away. While (Figure 5.c), and (d) needed nearly 24h. The three kinetics models with R2 values greater than 0.871 were selected to excite the experimental data (Table 3.5).

The pseudo-first-order model may explain why the adsorption rate decreases linearly as the adsorption capacity rises (Xiaolan Hu et al., 2018). The pseudo-second order kinetic model states that the contact between two reagent particles is rate-limiting, and that chemical adsorption mechanisms like electron sharing and electron transfer are used to address the adsorption rate (Xiaolan Hu et al., 2018). The Elovich model was created to explain the chemisorption of CO molecules in the first place (Zeldowitsch J. et al., 1934). As a result, the equation adequately explains the chemisorption of molecules such as $NH_4^+$-N and $NO_3^-$-N in this example (Paramasivam S. et al., 2018). The results imply that $NH_4^+$-N adsorption plays a considerable role in even monolayer ammonium adsorption, and that a pseudo-first-order rate equation was followed. Aside from that, the CBC-$NH_4^+$-N $q_e$ values increased.

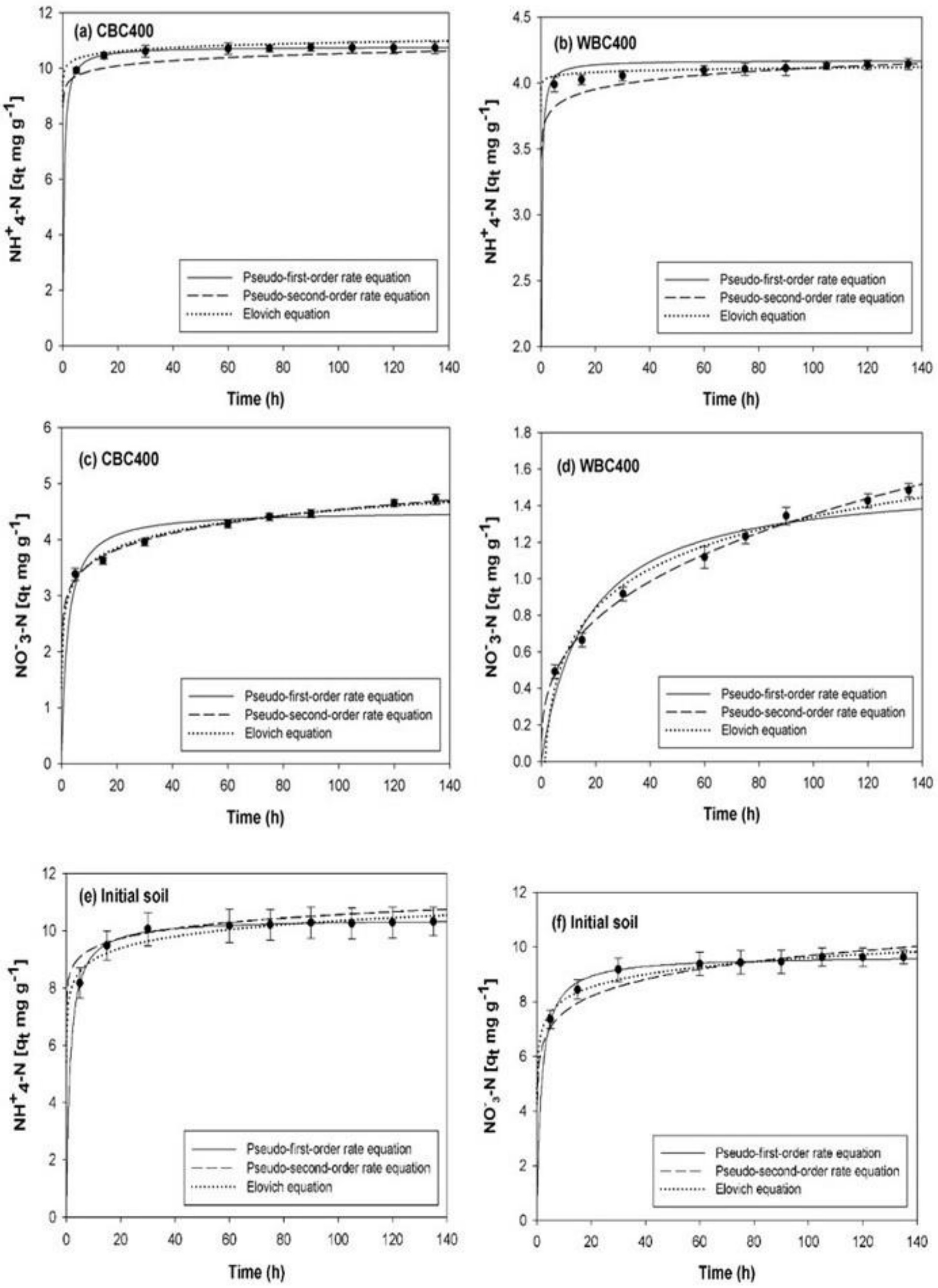


**Figure 3**. **7.** $NH_4^+$-N and $NO_3^-$-N Adsorption Kinetics on CBC400, WBC400 and Initial soil

### 3.3.6.3 Desorption kinetics of $NH_4^+$-N and $NO_3^-$-N onto CBC, WBC and Soils

As results of $NH_4^+$-N and $NO_3^-$-N release dynamic from biochar and soils are shown in (Figure 3. 8a) and (Figure 3. 8b). Within the 120 min, the $NH_4^+$-N release from CBC400 increase to 4.9 mg $g^{-1.}$ Similarly, $NH_4^+$-N release from initial soil increase to 9.0 mg $g^{-1}$. Beside of WBC the $NH_4^+$-N desorbed from WBC extremely slow, even though it pyrolysis the same condition 400 °C. Biochar showed lower desorption at levels of N loading concentration. Microporous surface of biochar and internal pores were utilized for loading of N by slow diffusion (Manikandan A. et al., 2013). While (Figure 3. 8b) $NO_3^-$-N release from WBC faster than CBC and initial soil by 10.87, 9.48, and 10.06 mg $g^{-1}$, respectively.

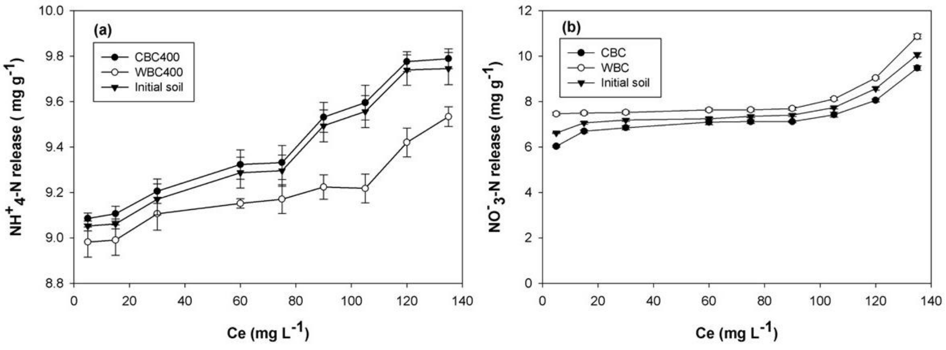


**Figure. 3. 8** $NH_4^+$-N and $NO_3^-$-N desorption onto CBC, WBC, and initial soils

# Summary

The initial pH of soil (6.55) is in a proper range for plant nutrient uptake whereas the initial pH of CBC, and WBC varied from moderately alkaline to alkaline. CBC and WBC produced similar yields which varied from about 32.49% to 33.93%, respectively. The percentage of ash content in CBC (2.9%) was lower than ash content in WBC (11.6%), however, its ash contents were in the average ranges. C/N ratio, ranging from about 52 for CBC and 312 for WCB, respectively. CBC and WBC had O/C and H/C ratios close to the recommendation thresholds, indicating well-pyrolysed ranges, enrichment of aromatic structures, and prone to degradation. The CEC of biochars were similar and were in the average ranges while CEC of the initial soil was in suitable for soil to hold and exchange cations in the soil solution, however, main elements in CBC, WBC, and the initial soil were exchangeable K, Na, and Ca, respectively. The similar strong peaks decreased at ~1350 and ~1600 $cm^{-1}$ of C=C and –COOH for both CBC and WBC were due to carbon condensation. BET specific surface area of biochars of WBC and CBC were low, however, SEM showed that WBC has more chance to enhance exposure of inorganic minerals as it increased in the pore structure comparing to CBC. $NH_4^+$-N The Langmuir isotherm model was better fitted to both biocahrs, with higher $r^2$ values than the Freundlich isotherm model (Gai X. et al., 2014). When compared to CBC, and WBC released more nitrogen from surface area. The adsorption of $NH_4^+$-N and $NO_3^-$-N are more suited to pseudo-first-order and pseudo-second-order kinetic models, respectively.

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# CHATPER 4

# EVALUATION OF BIOCHAR EFFECT ON INORGANIC NITROGEN AND PLANT GROWTH PRODUCTION UNDER PLOT CONDITIONS

## 4.1. Introduction

Soils store more carbon than both plants and the atmosphere combined, making them the world's biggest carbon (C) reservoir (Lehmann and Kleber, 2015). Discovered that pyrogenic carbon was produced by wildfires, intentional burning, or anthropogenic inputs such bio-char. Biochar has the potential to retain biomass carbon effectively in soil amendments, therefore enhancing soil fertility and crop growth. In recent years, biochar produced from agricultural waste has grown in popularity (Lehmann and Joesep, 2009; Kookann, 2010). Biochars have a lot of potential as a soil additive for improving soil fertility and sequestering carbon (Fanqi Jing et al., 2018). The adsorptive qualities of biochar are the focus of biochar's use in soils. Biochar's ability to absorb organic contaminants has been linked to its large specific surface area, well-developed pore structure, and diverse surface functional groups (Fanqi Jing et al., 2018). Other research has focused on carbon-based compounds such as activated carbon (Fanqi Jing et al., 2018). Biochar is a lower-cost method for recycling valuable products from residual biomass resources. Some researches employed Langmuir, Freundlich, and kinetics to characterize $NH_4^+$-N and $NO_3^-$-N adsorption isotherms and release on biochar, taking into account the effect of the source biomass and pyrolysis temperature.

Excessive nitrogen (N) fertilizer use can pollute surface and groundwater, causing eutrophication of aquatic organisms (Zhu A.N at al., 2005). After a few research shown that biochar can impact nitrogen availability and cycle, it is being investigated as a viable material to reduce N leaching in the soil (Galvez A. and Lehmann Joseph., 2013). However, there have been significant discrepancies in the research on the impact of biochar treatment on nitrogen leaching (Ding Y et al., 2010). At 0.20 m soil depth, there was a 15% decrease in $NH_4^+$-N leaching (Laird D et al., 2010). When biochar was added to the surface soil layer of typical US Midwestern agricultural soils, total nitrogen leaching was reduced by 11%. According to their results, they arrived at a decision. They determined that biochar might be utilized as a soil supplement to assist reduce nitrogen losses from soils due to its high potential for nitrogen absorption (Gai X. et al., 2014). Biochar's capacity to absorb NO3—N is also restricted or non-existent, according to certain research. Biochar produced from corn (Zea mays L.) or oak (Quercus spp.) had minimal NO3- adsorption capability and even discharged NO3- into aqueous solution, according to other investigations (Hollister CC et al., 2013; Yao Y et al., 2012; Gai X. et al., 2014). The disparities are most likely due to variances in biochar properties, necessitating more investigation into the connection between biochar qualities and $NH_4^+$-N and $NO_3^-$-N (Paramasivam S. et al., 2000) adsorption in the environment.

The molecular structure and size distribution of biochar (Xiapu Gai et al., 2014) can be influenced by the feedstock and pyrolysis temperature, thereby altering biochar sorption characteristics (Ofori-Boadu Andrea Nana et al., 2018). Biochars with varying surface areas, porosity, and functional groups have variable biochar sorption properties, and all of these variables have an impact on the sorption properties of biochar (Sohi et al., 2010, Gai X. et al., 2014). Despite being generated at the same temperature (400 °C), the poultry-litter biochar exhibited a higher specific surface area and porosity than the wheat-straw biochar (Sun et al., 2010; Gai X. et al., 2014). Biochar that has been pyrolyzed at a high temperature has a wider specific surface area and is more aromatic (Ahmad M et al., 2012). For instance, charcoal formed from wheat residue at temperatures between 500 and 700°C is substantially carbonized and has a large specific surface area (>300 m2 g-1), but chars made at temperatures between 300 and 400°C are only partially carbonized ( Gai X. et al., 2014), and have a smaller specific surface area than other (200 m2 g-1) (Chun Y et al., 2004; Gai Xiapu et al., 2014). Due to the comparatively stable aromatic backbone formed after pyrolysis and the increased number of C5O and C-H functional groups that may act as nutrient exchange sites following oxidation, low-temperature biochar (Gai Xiapu et al., 2014). (250–400 degrees Celsius) is anticipated to be more appropriate for soil fertility enhancement than high-temperature biochar (450 degrees Celsius) (Novak JM et al., 2009; Gai Xiapu et al., 2014). It was found that putting low temperature biochars into soil enhances soil fertility by enhancing the soil's capacity for cation exchange (CEC) (Liang B et al., 2006; Gai Xiapu et al., 2014).

Despite the fact that nitrate is slowly released from both soil-aged (Nikolas Hagemann, et al., 2017), and biochar-aged plants, biochar's interaction with mineral and organic nitrogen species, notably nitrate, has recently been postulated as a crucial mechanism for promoting biochar plant development (Haider G et al., 2016; Nikolas Hagemann, et al., 2017). Biochar that has been combined with compost feedstock is referred to as "co-composted." (i.e. nutrient-dense organic materials with labile organic carbon, such as manure) before aerobic composting (Fischer D et al., 2012). In comparison to mixing pristine/fresh biochar (no post-production treatment)

(Nikolas Hagemann, et al., 2017), with previously mature composting, this method produced a compost with greater agronomic quality (better plant growth promotion in pot experiments) (Kammann CI et al., 2015; Nikolas Hagemann, et al., 2017).

Plant accessible nitrate is typically quantified in soil or compost by extracting it for 1 hour with deionized water or a 2 M KCl solution (Maynard DG et al., 1993). According to, "slowly released nitrate $NO_3^-$-N" is defined as nitrate that is only released in subsequent extractions after a one-hour extraction (Kammann CI et al., 2015). For the time being, the underlying processes of "nitrate delayed release" are mainly unknown, and it is referred to as "nitrate capture."

The research presented in this chapter examines the release of ammonium ($NH_4^+$-N) and nitrate ($NO_3^-$-N) from two biochar-amended and a loamy soil throughout the first, second, and third years in a soil-mixture. Following repeated extractions with 1 M $NH_4Cl$ and $KNO_3$ of adsorption and desorption, ammonium and nitrate were measured. Through an adsorption kinetics experiment, we evaluated with two extraction settings to understand more about the mechanics of ammonium and nitrate capture and release. The main objectives are to conduct adsorption and desorption tests using biochar which is aged in the soil system by (1) determining the effects of chemical aging on biochar properties, (2) investigating the impact of biochar on soil (Laetitia H. et al., 2019) quality over a two-year period, with a focus on soil nitrogen (N), and (3) investigating the effect of nutrients on growth and production of plants in soil system (Wael M. S. et al., 2019).

## 4.2. Materials and Methods

### 4.2.1. Plot design with plant growth experimental process

The plot test for 52 days planting period and took place in a loop top garden at building #35, Seoul National University, South Korea. Following the application of coffee grind biochar (CBC) and wood chip biochar (WBC), the leaf length, leaf width, root length, and total biomass were parameter measured. Pak Choi (Brassica rapa chinensis L.) was grown in triplicate in a loamy soil with dosage levels of 0, 2.5, and 5.0 percent w/w in a randomized complete block design with three duplicates. CBC and WBC were produced through pyrolysis at 400 °C for 2 h.

### 4.2.2. Biochar production aged for one, two, and three years

Biochars made from coffee ground (CBC), and wood chip9WBC) were used individually, and each plot was tested separately. From the 1st of May to the 22nd of June, Pak choi species was grown in sandy loamy soil on the loop top of a building at Seoul National University for three seasons: 2018, 2019, and 2020. (Table 4.1). In order to make easy to use with a short instead in term of each year such and 1st Year, 2nd Year, and 3rd year respectively. We also did a four-year application of cultivation known as confirmation crop growth.

Prior to being immobilized, the coffee grinds (CBC) and woodchips (WBC) were oven dried for 48 hours at 105°C. The biochars were made at a pyrolysis temperature of 400 degrees Celsius and then combusted for 2 hours at a heating rate of 5 degrees Celsius per minute in an automated biomass paralyzing furnace (TH-01, Germany). Biochars were crushed to pass through a 2-mm screen after the pyrolysis process before being put into soils.

### 4.2.3. Measurement of Main Elements

#### 4.2.3.1 pH of CBC400, WBC400, and soils

Biochar and soil pH were measured in 1:20, and 1:5 biochar: water (deionised water; deionized water) ratio after 1 h shaking, and 1:5 soil: water ratio after 24 h shaking on a reciprocating shaker with a tube rotator in room temperature at 25°C. pH buffers of 7 and 10 were used to calibrate the pH meter. After 1 hour of shaking and 30 minutes of equilibration time, the pH of the reference biochar and soil samples were determined in 0.01 M $CaCl_2$ using a 1:10 and 1:20 biochar: $CaCl_2$ ratio. 5 g biochar and 10 mL distilled water were used in the biochar and soil doses.

#### 4.2.3.2 Soil sampling and total organic carbon (SOC) total soil nitrogen(TN) and measurements

Every seasonal crop, soil-mixture samples were taken from 0 to 20 cm depth (Yang C. et al., 2005) from each plot using a core sampler. To make a composite sample, three core samples were obtained at random and homogenized. This sample was kept at 5 degrees Celsius and used for testing. The quantity of organic (SOC) and total nitrogen (TN) in the soil was measured using an elemental analyzer (EA). In a nutshell, 1.0 g of samples were crushed to pass through a 2 mm sieve before being fed into a high-temperature (1,000 °C) furnace and burned in pure oxygen under static circumstances. Carbon was transformed to carbon dioxide, hydrogen to water, nitrogen to nitrogen gas/nitrogen oxides, and sulphur to sulphur dioxide throughout the combustion (Akoji. J. N. et al., 2019) process. After passing the gases through absorbent traps to remove all but carbon dioxide, water, nitrogen, and sulphur dioxide, the gases were detected and (Akoji. J. N. et al., 2019) recorded. The weight percent of each element was calculated.

### 4.2.4 Adsorption and desorption experiment

**Adsorption isotherm**

As batch adsorption experiments under isotherm were carried out to investigate the $NH_4^+$-N and $NO_3^-$-N adsorption kinetics onto coffee grounds and woodchips biochar. In all, 100 mL of $NH_4Cl$ and $KNO_3$ solution were produced in a 100 mL conical glass flask and shaken for up to 120 minutes at 25°C on a rotatory shaker at 60 rpm. The suspension (0.1 mL) were collected at 5, 15, 30, 60, 75, 90, 105. And 120 minutes. Solid mass loss was minimal over sampling time because the solids in the suspensions were rapidly separated from the liquid phase. The solutions were tested for $NH_4^+$-N and $NO_3^-$-N using an ultra-spectrophotometer after passing through a 0.45 mm Millipore filter. $NH_4^+$-N and $NO_3^-$-N concentrations were determined using an ultraviolet wave spectrometer (HS-3300, Republic of Korea, HUMAS Co., Ltd) (Rahil, M. H. et al., 2007; Park M. H. et al., 2019). The Nessler technique and the Chromatropic acid method, with slight modifications, were used to detect $NH_4^+$-N and $NO_3^-$-N (Rahil, M. H. et al., 2007) concentrations in samples (Park M. H. et al., 2019). The $NH_4^+$-N and $NO_3^-$-N starting concentrations were 50 ml L-1, and 0.5 g of biochar was added to the solution (Park M. H. et al., 2019) at 25°C and manually stirred at 60 rpm using a tube rotator (Park M. H. et al., 2019). On a regular basis, the concentration of an aliquot of solution (0.5 mL) was checked. The concentrations of $NH_4^+$-N and $NO_3^-$-N were determined using the following methods:

$$q_e = \frac{(C_0 - Ce).V}{M} \quad (1)$$

where $q_e$ denotes as the adsorbed and desorbed mass of $NH_4^+$-N and $NO_3^-$-N in (Ojeda, G. et al., 2006) mg $g^{-1}$ per unit mass of biochar. $C_0$ is the initial $NH_4^+$-N and $NO_3^-$-N concentration in mg L1, and Ce is the equilibrium $NH_4^+$-N and $NO_3^-$-N concentration in mg $L^{-1}$. M denotes as the dry mass of biochar in grams, and V is the volume of $NH_4^+$-N and $NO_3^-$-N solution in L. Each of the aforementioned adsorption experiments was repeated three times. The removal efficiency of $NH_4^+$-N and $NO_3^-$-N was calculated (Liu, X. et al., 2006) using the following equation.

$$R_e = \frac{(\ C_0 - \ C_e).100}{C_0} \quad (2)$$

where Re denotes the $NH_4^+$-N removal efficiency in percent, and $NO_3^-$-N denotes the $NO_3^-$-N removal efficiency in percent.

## 4. 2. 5 Adsorption and desorption Kinetics

### 4.2.5.1 Adsorption kinetics

The $NH_4^+$-N and $NO_3^-$-N adsorption kinetics onto coffee grounds and woodchips biochar were studied in a batch adsorption experiment under isothermal conditions. In a 100 mL conical glass flask, 100 mL of $NH_4Cl$ and $KNO_3$ solution was prepared and agitated for up to 120 minutes at 25°C on a rotatory shaker at 60 rpm. At 5, 15, 30, 60, 75, 90, and 105 minutes, the suspension (0.1 mL) was collected. In addition, there are 120 minutes. Because its particles in the suspensions were promptly separated from the liquid phase, the solid mass loss was minimal throughout sampling time s. The solutions were analyzed for NH4+-N and NO3—N using an ultra-spectrophotometer after passing through a 0.45 mm Millipore filter.

The starting concentrations of $NH_4^+$-N and $NO_3^-$-N were 50 ml $L^{-1}$ (Ojeda, G. et al., 2006). The temperature was set at 25°C, and 0.5 g of biochars was added to the solution (Park M. H. et al., 2019), which was then manually stirred at 60 rpm using a tube rotator (Park M. H. et al., 2019. The concentration of an aliquot of the solution (0.5 mL) was measured on a regular basis. $NH_4^+$-N, and $NO_3^-$-N concentrations of were measured using equation as below:

$$q_t = \frac{(\ c_0 - \ C_t).V}{M} \tag{3}$$

where $q_t$ denotes as the mass of $NH_4^+$-N and $NO_3^-$-N adsorbed and desorbed per unit mass of biochar (Gai X. et al., 2014) at time *t* in mg $g^{-1}$.

### 4.2.5.2 Desorption kinetics

The remaining solution in the tubes was decanted after the adsorption experiment, and 50 mL of distilled water was poured as directed for the desorption experiment as followed the adsorption method. This technique was repeated 10 times every three days, yielding two phases of desorption. Within 24 hours, the ammonium N concentration in the supernatant was determined using a continuous flow analyzer.

### 4.2.5.3 Repetitive $NH_4^+$-N and $NO_3^-$-N extraction

Following releasing kinetics experiment, biochar samples were filtered out of the deionized water and new water was added every three days to release N for the following ten days. The kinetics and release tests were repeated three times, with the average results and standard deviations provided each time.

## 4.2.6. Effects of aged CBC and aged WBC on crop yields

The whole samples plant from plot tests were selected from an entire plot experiment and harvested 52 days and store under 5 ˚C in the refrigerator for three to five days to measure the wet weight and dry weight of biomass at 105 ˚C for 24h.

### 4.2.7. Analytical methods

#### 4.2.7.1 Biochars and soils properties

The data was statistically analyzed using the student t-Test with a notable difference ($p < 0.05$) threshold. The influence of biochar and feedstock treatments on aged CBC and WBC, as well as soil application.

The average of three replications was used for adsorption and desorption tests. The Elovich model was examined using Sigmaplot version 10.0 and a one-way analysis of variance. Adsorption data were fitted to Freundlich and Langmuir isotherms, and (Wei-Yu Lai et al., 2013) kinetics models included Pseudo-first-order and second-order equations (ANOVA). All data was examined for normality by treatment, and the statistical significance of differences in treatment averages was determined using Duncan's multiple range test. Before doing statistical comparisons, three replicates were employed. At the (*p* –values < 0.05 level), Tukey's test was employed to check if there were any significant differences between the amendment means.

## 4.3. Results and discussion

### 4.3.1. Plot design and plant growth experimental process

#### 4.3.1.1 Preparation of experimental lots

This study was conducted at Seoul National University (SNU) in the Republic of Korea from May 1 to June 22, 2018, 2019, and 2020 and 2021 as conformational crop yields. The effects of coffee ground and woodchip biochars on

Pak choi (*Brassica rapa var. chinensis* L.) crop production were investigated using a plot test and a laboratory research. The availability of nutrients in the soil after using biochars, as well as the nutritional value of crop development, were evaluated. A fully randomized block design (CRBD) was used in the experiment, with three replicates for each type and treatment. The experiment was conducted with the plot's size of 0.32 m X 1.0 m (0.32 m$^2$) that plot had been ploughed to a depth of 20 cm. Plough to land preparation before planting and lies for 3-5 days under sunlight in this experiment, Treatment control was the untreated biochar (T-0), in Treatment 1 (T-1) was the soil with biochar at 2.5 % (w/w), Treatment 2, soil with biochar at 5.0% (w/w) (T-2) in (Table 4.1). Biochar was applied by spreading the material on the soil surface and incorporating using a rake. In addition to biochar, CBC and WBC were applied to all six treatments at a dose of 2.5 and 5.0% (w/w), respectively.

**Table 4.6.** Biochar doses, year of designed plots and planting period

| Plant | CBC & WBC (%), (w/w) | Year of application | Planting period |
|---|---|---|---|
| Pak choi | 0.0, 2.5, and 5.0 | 2018, 2019, 2020 | 52 days ( 01 May – 22 June) |

* CBC (Coffee grounds biochar), * WBC (Woodchips biochar)

#### **4.3.1**.2 **Plant material and cultivation**

The Pak choi variety was used in this experiment at the loop top lot experiment of Seoul National University (SNU), Korea. Firstly, the seeds were sown direct to the entirely plots test and put five seeds were applied into holes (Figure 4.1). The total 12 holes per plot with spacing from 15 cm per each crop. Watering was based on the temperature. Temperature < 26 °C was provided one time per day. We watering two times a day in case of the temperature between 25 ˚C to 38 °C. Appropriate temperature was between 25-38 °C, (Lee et al., 2003). After two weeks, removed the weeds and turned the soils. Pak choi take 52 days to reach maturity.

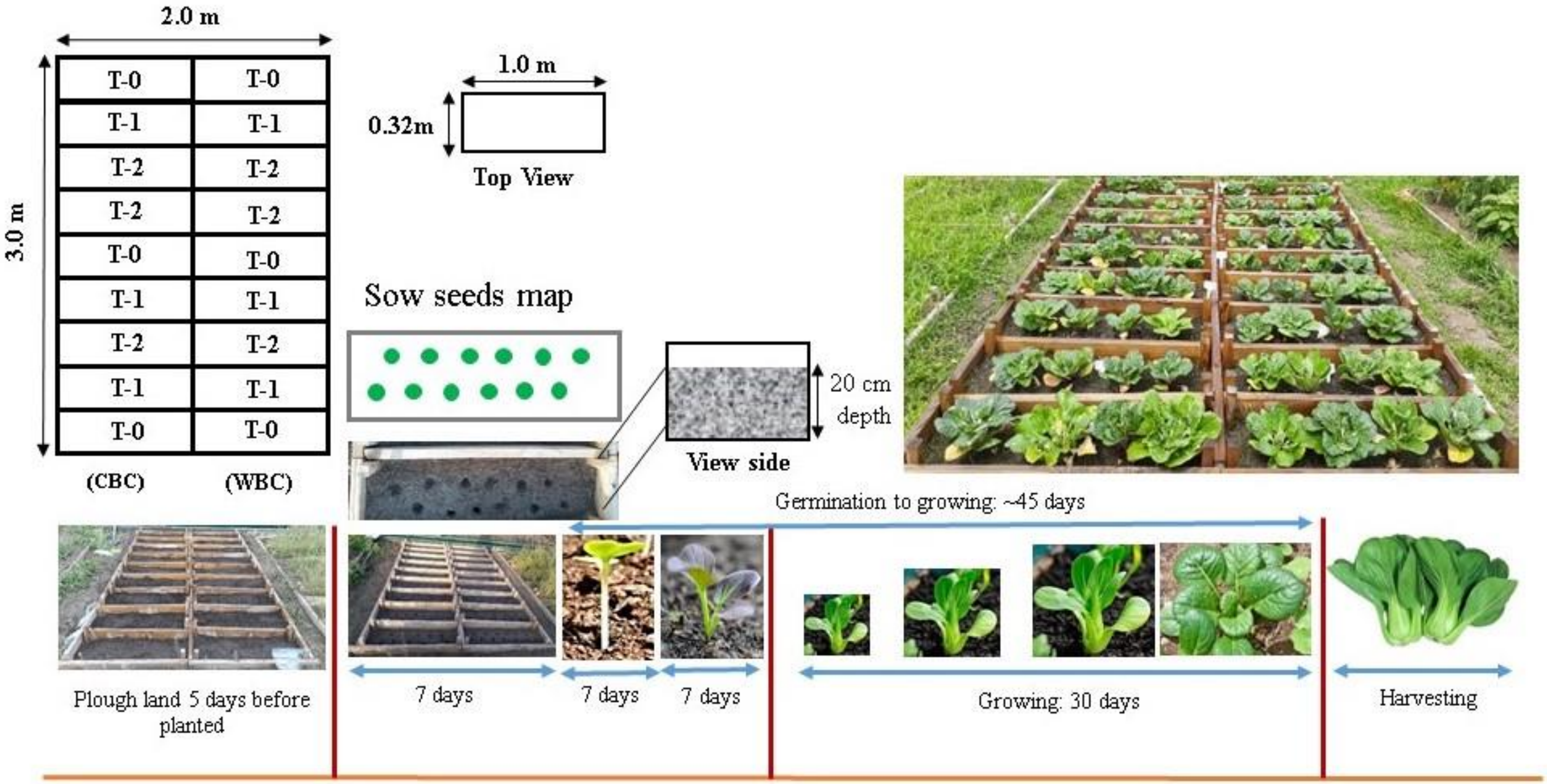


**Figure.4. 9**. Sketch map of the experimental area horizontal layouts and plant growth process

### 4.3.2. pH of aged CBC, aged WBC, and soils application

Table 4.6 demonstrates that in the second year, CBC did not show a noticeable difference *p*-values > 0.05 in aged BC, but in the third year, it did show a noticeable difference *p*-values < 0.05 when compared to the first year. However, when all treatments were compared to control over the course of a year, there was a substantial change in soil-mixture. WBC indicated a significant difference in dosages biochar application in treatments, with a *p*-values < 0.05 significance level. This is due to the fact that in deionized water, active functional groups in soil media were not separated. The elevated pH in this experiment could be a result of an increase in soil pH caused by solitary biochar application.

Higher pH of CBC, WBC 9.32, and 8.47 was probably due to ash accretion while amended soil (Table 4.7). Carbonates alkali and alkali earth metals are heavily represented in ash residues. Therefore, increasing soil pH can improve soil quality by biochar application. To improve the pH of acidic soils, biochars could be utilized as a substitute for lime materials.

**Table 4.7.** pH of Soil mixed with CBC and WBC at the harvested

| **Treatments** | **Soil from CBC plot test** | | | | **Soil at WBC plot test** | | | |
|---|---|---|---|---|---|---|---|---|
| **% (w/w)** | **1Year** | **2 Years** | **3Years** | **4 years** | **1Year** | **2 Years** | **3Years** | **4 years** |
| **Control** | 6.1 ± 0.1 | 6.2 ± 0.0 | 6.2 ± 0.1 | 6.40±0.08 | 6.3 ± 0.17 | 6.4 ± 0.04 | 6.20 ± 0.12 | 6.32±0.04 |
| **2.5** | 7.5 ± 0.3 | 7.5 ± 0.1 | 7.6 ± 0.1 | 6.59±0.03 | 7.2 ± 0.14 | 7.6 ± 0.25 | 7.65 ± 0.19 | 6.36±0.02 |
| **5** | 7.6 ± 0.1 | 7.2 ± 0.0 | 7.6 ± 0.2 | 6.50±0.02 | 7.4 ± 0.06 | 7.5 ± 0.05 | 7.67±0.09 | 6.32±0.03 |

### 4.3.3. Extractable cations of Ca, K, Mg, and Na in soils on seasonal crop

Following the application of biochar to the soil, (Ding Yang et al., 2016) number of exchangeable cations and nutritional elements such as Na, K, Ca, and Mg

(Ding Yang et al., 2016) may be increased, thereby increasing cation exchange capacity and nutrient availability (Figure.4.9). In (Figure. 4.9a), Ca and K were increased by 912 to 9.2 mg. g$^{-1}$ for all years of soils-mixture CBC compared to control, while Mg and Na were slightly increased by 2.13 to 2.42 mg. g$^{-1}$ and 1.6 to 1.66 mg. g$^{-1}$ (Ding Yang et al., 2016) respectively. In (Figure. 4.9b), Ca and K were increased by 8.51 to 9.10, and 7.32 mg. g$^{-1}$, respectively. However, Mg and Na was not increased 2.18 to 2.77, and 0.30 to 1.120 mg g$^{-1}$. While (Figure. 4.9c) the three years' soil-mixture CBC was increased Ca, and K by 8.74 to 9.89, and 7.55 to 8.83 mg g$^{-1}$, respectively.

Regarding soil-mixture WBC 400 for three years in (Figure 4.9d), (Figure 4.9e), and (Figure 4.9f), treatment1(T-1) and treatment-2 had increased Ca and K by 8.0 mg g-1 to 8.75 and 5.62 to 9.47 mg g-1, 6.2 to 4.86 for the second year, and 4.86 to 8.58 mg g-1 for the third year of soil-mixture WBC respectively. But Soil-mixture WBC was not increased Mg and Na all three years of woodchip biochar applications. According to the findings, quantity of extractable K, Ca, Na, and Mg increased by 60 to 670 percent after charcoal was added. The amount of potassium in the soil has grown from 42 to 324 mg kg$^{-1}$ (Ding Yang et al., 2016). Additionally, biochar treatment also enhanced saturated hydraulic conductivity from 16.7 to 33.1 cm h$^{-1}$ and increased base saturation percentage from 6.4 to 26 percent (Ding Yang et al., 2016), the rate of soil erosion was reduced from 1458 to 532 g m$^{-2}$ h$^{-1}$, total carbon was increased from 2.27 to 2.78 percent, total nitrogen was raised from 0.24 to 0.25 percent, and accessible phosphorus was enhanced from 15.7 to 15.8 mg kg$^{-1}$ (Jien and Wang 2013; Jones et al., 2012; and Ding Yang et al., 2016).

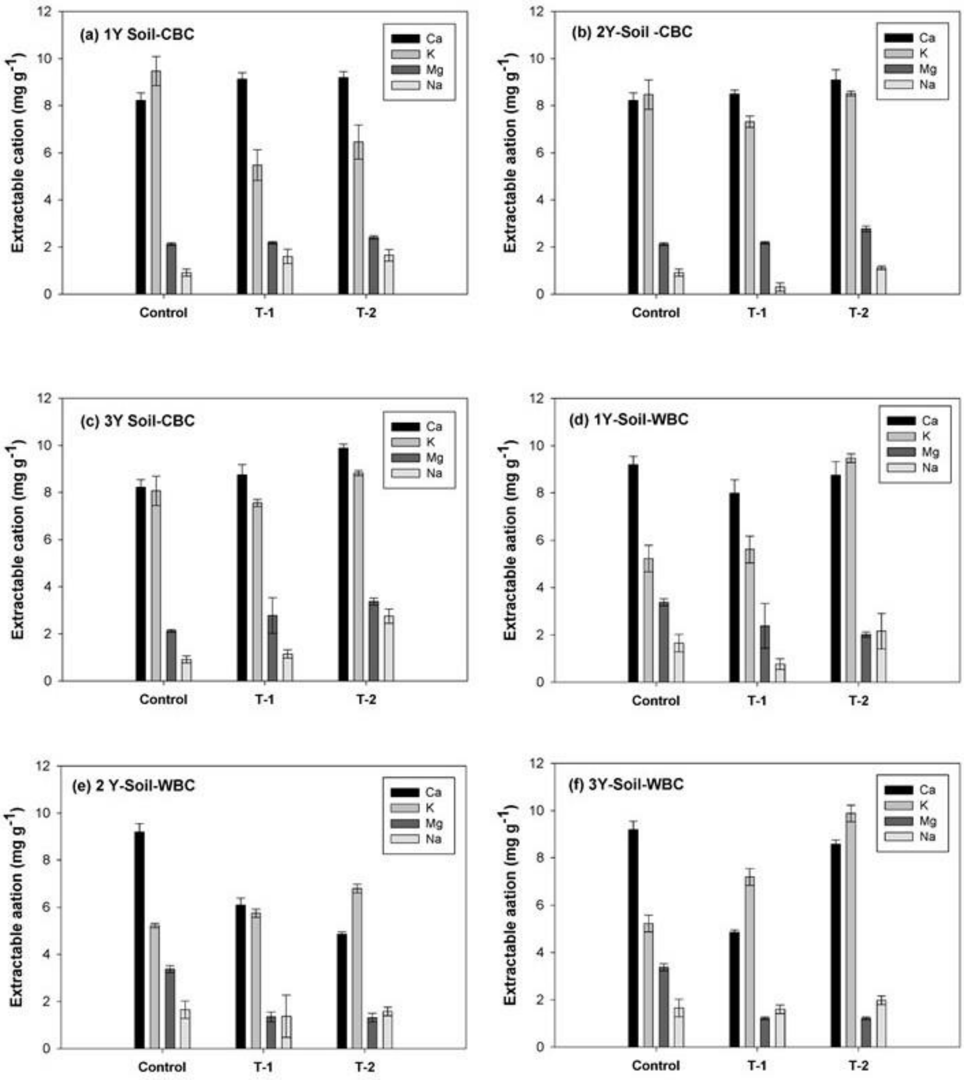


**Figure. 4.9**. Extractable cations in soil application in lot test of CBC Fig.2(a), (b), (c), and Fig.2(e), (d), and (f), WBC soil from lot test of CBC as a first year, second year, and third year after harvested.

These changes in the chemical properties of the soil may result in an increase in soil fertility as a result of the increased nutrient content and availability as a result of these changes. However, not all changes in the physical or chemical characteristics of the soil were detected (Ding Y. et al., 2016). After three years of biochar addition, soil electrical conductivity (which decreased from 46 to 43 S cm-1) and bulk density (which increased from 1.04 to 1.08 g cm-1) did not differ substantially from baseline values (Ding Y. et al., 2016) modified in a UK research study (Jones et al. 2012). Even in the same experiment, biochar appeared to enhance soil physical quality in the first year after application, increasing porosity, improving soil aggregation, and lowering soil bulk density (Nelissen et al., 2015). In the second year after biochar application, (Nelissen et al., 2015) found no difference in hydraulic conductivity or plant available water capacity. Furthermore, biochar treatment had no substantial impact on soil chemical characteristics during a two-year period. Additionally, with the exception of organic carbon content and the C:N ratio (Ding Yang et al., 2016), biohcar treatments showed no significant effect on soil chemical characteristics after two years ( Nelissen et al., 2015).

According to the findings of this study, the effects of coffee ground and woodchip biochars on soil physical and chemical properties vary depending on the (Pokharel, P. et al., 2019) application circumstances. Long-term field trials are required to determine whether biochar treatment can permanently alter soil qualities. Overall, changes in soil characteristics may enhance nutrient content of Ca and K availability while decreasing nutritional Mg and Na leaching, both of which are established methods for increasing soil fertility.

### 4.3.4. Analysis total extraction of heavy metals of biochars and soil-mixture

Table. 4. 8 Heavy metal of soils, CBC, WBC and soil- mixture.

| **Heavy metal** | **Soil** | **CBC** | **WBC** | **Soil-mixture-CBC** | | **Soil-mixture-WBC** | |
|---|---|---|---|---|---|---|---|
| | | | | **2.5%** | **5.0%** | **2.5%** | **5.0%** |
| Cd (mg kg-1) | 0.03 | nd | nd | 0.03 | 0.03 | 0.03 | 0.03 |
| Cu (mg kg-1) | 0.99 | nd | nd | 1.78 | 1.94 | 3.32 | 2.22 |
| Pb (mg kg-1) | 0.04 | nd | nd | 0.31 | 0.41 | 0.4 | 0.45 |
| Zn (mg kg-1) | 5.99 | 0.25 | 0.3 | 4.95 | 4.87 | 5.18 | 5.35 |

As table shown that Zn and Cu of soil and soil-mixture with CBC and WBC (dose of 2.5% and 5.0% by weight maintains heavy metal by 5.99 and 0.99, 4.95 and 1.78, 4.87, and 1.94, 5.18, and 3.32, and 5.35 and 2.22 mg kg$^{-1}$. it was co-enzyme for plant growth. However, the heavy metal Cd, and Pb was not shown any provoke a significant effected of concentration of heavy metal in biochars added in soils.

The findings, the Cu, and Zn was high concentration in soils and useful for plant growth.

### 4.3.5. Adsorption isotherms and kinetics

#### 4.3.5.1. $NH_4^+$-N Adsorption isotherm on CBC400 and WBC400

To assess the $NH_4^+$-N and $NO_3^-$N adsorption/desorption capability of aged biochars, in triplicates, a series of batch sorption and desorption experiments were conducted. We have varieties of aged biochars for one year, two years, and three years biochar: coffee ground and woodchip biochars.

The Langmuir and Freundlich sorption isotherms ($NH_4^+$-N) and nitrate ($NO_3^-$-N) concentration on maximum adsorption capacity of (Rahil, M.H et al., 2007) biochars were fitted to examine the effects of beginning ammonium in Table 4. Table 4.7 shows that the Langmuir and Freundlich sorption isotherms match quite well, as evidenced by strong correlation values ($R^2$).

The adsorption capacity of one-year-old biochars and two-year-old biochars rose fast in response to increases in initial $NH_4^+$-N and $NO_3^-$-N concentrations, then tended to stabilize with time longer than 120 minutes with biochar approaching saturation was obverse in Figure. 5.

As Table 4.7 shown, the values constant related to binding energy ($Q_{max}$) for $NH_4$-N adsorption (36.53 mg/g) and value $R^2$ (0.9999) of three years aged CBC was greater than two years and three years WBC (23.294 mg/g and 23.187 mg/g) and values ($R^2 = 0.996$, and 0.9995, respectively). Both Langmuir and Freundlich models were good predictors for $NH_4^+$-N and $NO_3^-$-N sorption isotherms. This is owing to ion competition (with H+ and OH-, respectively) and/or a change in surface charge, and both $NH_4^+$-N and $NO_3^-$-N sorption of aged biochar happens via competitive electrostatic ion exchange processes.

**Table. 4.9.** Langmuir and Freundlich parameters for adsorption of $NH^+_4$-N onto 1, 2, and 3 year(s) of aged coffee grounds and woodchips biochars

| **Sample** | **Langmuir isotherm** | | | **Freundlich isotherm** | | |
|---|---|---|---|---|---|---|
| | **$q_{max}$ (mg/g)** | **b (L/mg)** | **$R^2$** | **$K_f$ (mg/g)(L/g)$^n$** | **n** | **$R^2$** |
| 1 Year CBC $NH^+_4$-N | 17.108 | 0.0013 | 0.998 | 0.069 | 1.357 | 0.993 |
| 2 Years CBC $NH^+_4$-N | 6.706 | 0.0041 | 0.987 | 0.157 | 1.834 | 0.991 |
| 3 Years CBC $NH^+_4$-N | 36.527 | 0.0055 | 0.9999 | 1.541 | 2.158 | 0.977 |
| 1 Year WBC $NH^+_4$-N | 5.177 | 0.0080 | 0.985 | 0.373 | 2.556 | 0.958 |
| 2 Years WBC $NH^+_4$-N | 23.294 | 0.0017 | 0.996 | 0.150 | 1.458 | 0.990 |
| 3 Years WBC $NH^+_4$-N | 23.187 | 0.00184 | 0.9995 | 0.165 | 1.473 | 0.993 |

$q_{max}$= Maximum capacity, b = Langmuir constant, $K_f$ = Freundlich constant, n = desorption intensity

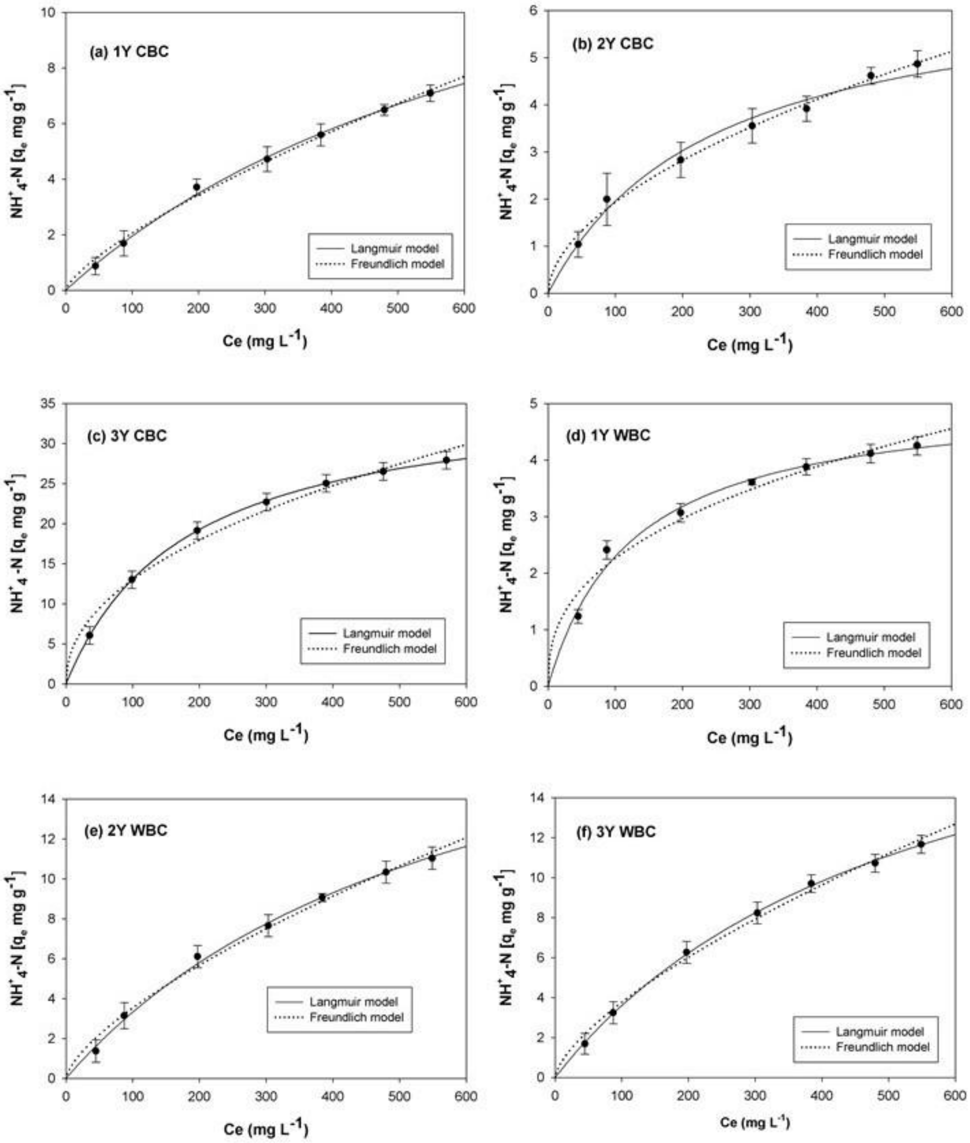


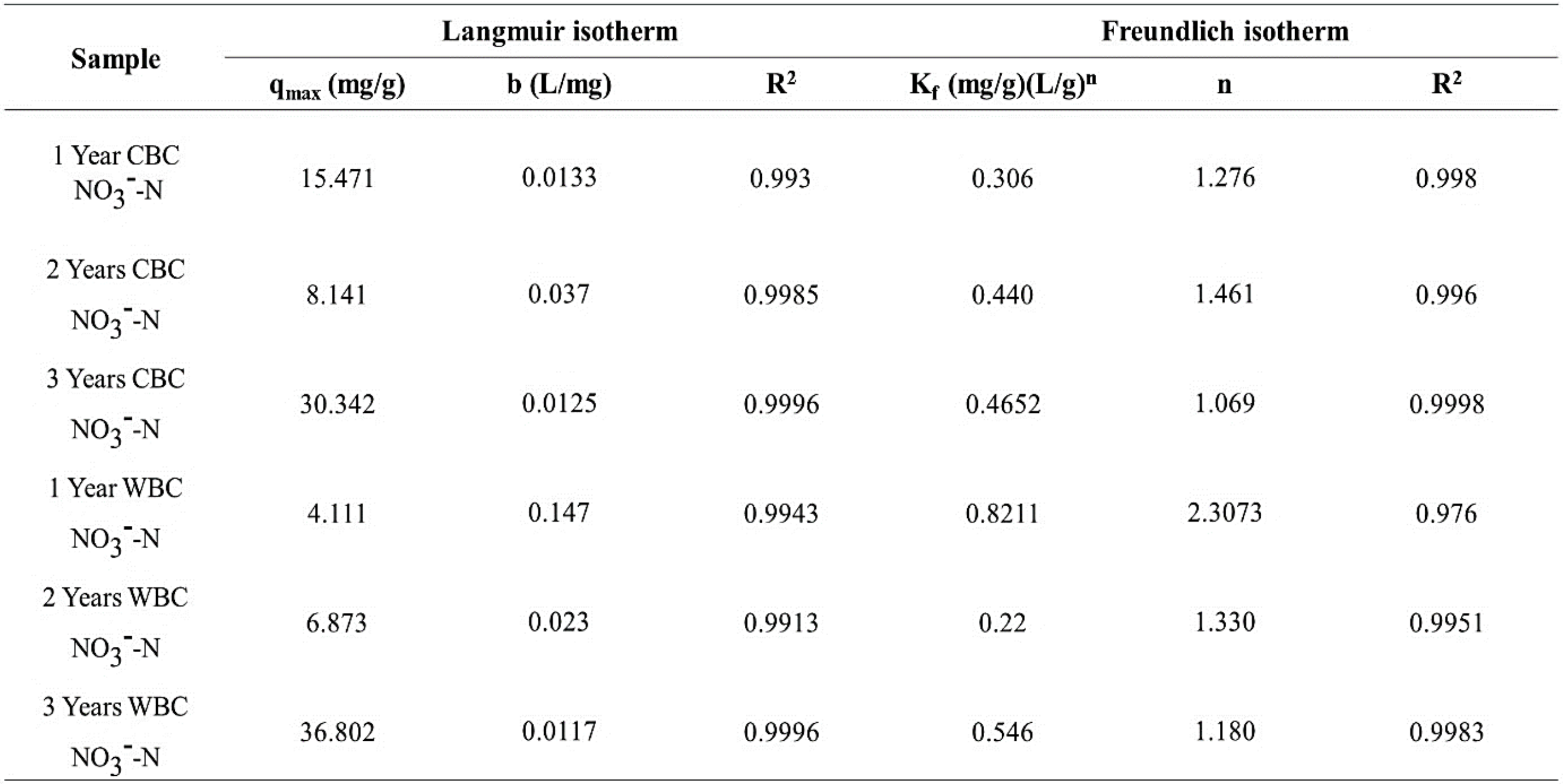
**Figure. 4.10.** Adsorption parameters by Langmuir and Freundlich of $NH_4^+$-N onto one, two, and three year(s) of aged coffee grounds and woodchips biochars

Both the Langmuir and the freundlich models were found (Wei-Yu Lai et al., 2013) to be well fitted to the data in the study. The adsorption isotherms of biochar to $NH_4^+$-N and $NO_3$—N were explained using the Langmuir and Freundlich models (Figure. 4.10). The Langmuir model (Wei-Yu Lai et al., 2013) is largely concerned with the adsorption of a single molecule layer by a single molecule layer (Xue, G et al., 2013). This model assumes that the adsorbents' surfaces are identical, and that each surface molecule or atom with a residual valence force adsorbs a gas molecule, resulting in a single layer of gas molecules adsorbing on the solid surface. Furthermore, adsorption is dynamic, with the adsorbed molecule having the ability to return to the gas phase when heated; As a result, the adsorption process is comparable to gas condensation, while the desorption process is similar to liquid evaporation. The Freundlich model is a hypothesis-free empirical equation. The value of 1/n is typically between 0 and 1. The intensity of the effect of concentration on adsorption capacity is indicated by the value of 1/n (Wang, P et al., 2017).

#### 4.3.5.2 $NO_3^-$-N Adsorption isotherm on CBC and WBC

Table 4.8 shows that three years biochar adsorption $NO_3^-$-N on aged WBC400 values qmax was 36.802 to 30.342 mg g-1 higher than three years aged CBC. When compared to CBC for years of soil-mixture, biochar's surface area of three years of WBC was shown to be higher. The influence of initial ammonium ($NH_4^+$-N) and nitrate ($NO_3^-$-N) concentrations on biochar maximum adsorption capacity was evaluated using the Langmuir and Freundlich (Wei-Yu Lai et al., 2013) sorption isotherms (Table 4.8). The Langmuir and Freundlich sorption isotherms were well-matched, as shown by significant correlation coefficients above values ($R^2$) = 0.99, as shown in Table 4.8.

**Table. 4.10.** Langmuir and Freundlich parameters for adsorption of $NO^{-}_{3}$-N onto 1, 2, and 3 year(s) of aged coffee grounds and woodchips biochars



| Sample | Langmuir isotherm | | | Freundlich isotherm | | |
|---|---|---|---|---|---|---|
| | $q_{max}$ (mg/g) | b (L/mg) | $R^2$ | $K_f$ (mg/g)(L/g)$^n$ | n | $R^2$ |
| 1 Year CBC $NO_3^-$-N | 15.471 | 0.0133 | 0.993 | 0.306 | 1.276 | 0.998 |
| 2 Years CBC $NO_3^-$-N | 8.141 | 0.037 | 0.9985 | 0.440 | 1.461 | 0.996 |
| 3 Years CBC $NO_3^-$-N | 30.342 | 0.0125 | 0.9996 | 0.4652 | 1.069 | 0.9998 |
| 1 Year WBC $NO_3^-$-N | 4.111 | 0.147 | 0.9943 | 0.8211 | 2.3073 | 0.976 |
| 2 Years WBC $NO_3^-$-N | 6.873 | 0.023 | 0.9913 | 0.22 | 1.330 | 0.9951 |
| 3 Years WBC $NO_3^-$-N | 36.802 | 0.0117 | 0.9996 | 0.546 | 1.180 | 0.9983 |

$q_{max}$= Maximum capacity, b = Langmuir constant, $K_f$ = Freundlich constant, n = desorption intensity.

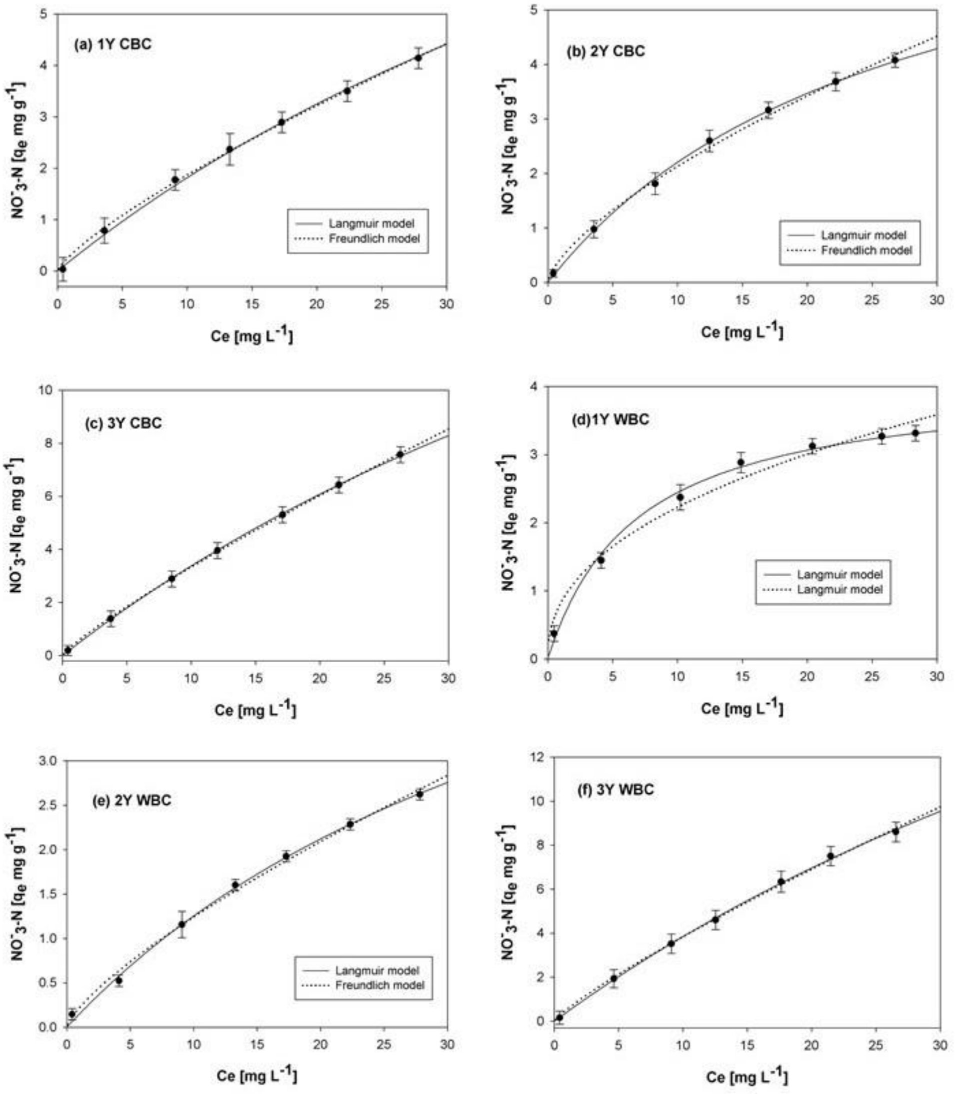


**Figure. 4.11** Adsorption parameters by Langmuir and Freundlich of $NO^{-}_{3}$-N onto 1, 2, and 3 year(s) of aged coffee ground and woodchip biochars.

The findings revealed that the Langmuir model best represents the adsorption process of a single molecular layer of saturation for aged biochars absorbing $NO_3$-N in a single molecular layer of saturation (Figure.10).

#### 4.3.5.3. $NH^+_4$-N and $NO_3^-$-N adsorption kinetics on aged CBC, WBC and soils

As shown in Table 4.9, $q_e$ represents the equilibrium adsorption capacity (mg $g^{-1}$), $k_1$ denotes as the pseudo-first-order rate constant (in $min^{-1}$) (Park M. H. et al., 2019), the constant of pseudo-second-order rate is denoted by k2 (in g $mg^{-1}$), *a* refers to the constant of Elovich for desorption in (mg $g^{-1}$ $h^{-1}$), and $\alpha$ is the constant of Elovich proportional to the initial rate of adsorption in (mg $g^{-1}$ $h^{-1}$) (Park M. H. et al., 2019). The adsorption of $NO_3^-$-N is described using the pseudo–first–order rate equation (Park M. H. et al., 2019) by biochar and soils, whereas the pseudo–second–order rate equation is utilized to analyze chemical adsorption processes (Wenliang Zhang et al., 2021)., whereas the Elovich equation is used to describe the chemisorption of carbon monoxide. The adsorption kinetics and fitted values are demonstrated in Table 4.9. The Pseudo-first order model has the strongest correlation (Lai Wei-Yu et al., 2013) coefficient ($R^2 > 0.94 – 0.99$). According to the findings, $NH_4^+$-N and $NO_3^-$-N adsorption CBC is a composite reaction involving external liquid film diffusion and surface adsorption (Tong, Y. et al., 2019), implying that it is a physical–chemical process. Furthermore, the physical importance of parameter of Pseudo-first-order, Elovich models is identified to effect the model coefficient, adsorption capacity $q_e$, initial adsorption rate, and $k_2$ constant rate.

**Table.4.11.** Adsorption kinetics model parameters for $NH_4^+$-N and $NO_3^-$-N adsorption on aged CBC

| Sample | Pseudo-first-order rate equation | | | Pseudo-second-order rate equation | | | Elovich equation | | |
|---|---|---|---|---|---|---|---|---|---|
| | $q_e$ (mg $g^{-1}$) | $k_1$ ($h^{-1}$) | $r^2$ | $q_e$ (mg $g^{-1}$) | $k_2$ (g $gm^{-1}$ $h^{-1}$) | $r^2$ | a | $\alpha$ | $r^2$ |
| 1Year aged CBC $NH_4$-N | 2.708 | 0.049 | 0.991 | 0.395 | 2.614 | 0.983 | 0.379 | 1.741 | 0.993 |
| 2Years aged CBC $NH_4$-N | 2.524 | 1.921 | 0.859 | 0.982 | 4.909 | 0.992 | 0.695 | 2.571 | 0.972 |
| 3Years aged CBC $NH_4$-N | 2.939 | 0.090 | 0.952 | 0.700 | 3.372 | 0.997 | 0.094 | 1.762 | 0.990 |
| 1Year aged CBC $NO^{-}_{3}$-N | 4.500 | 0.034 | 0.967 | 0.503 | 2.356 | 0.941 | 0.899 | 1.048 | 0.962 |
| 2Years aged CBC $NO^{-}_{3}$-N | 4.331 | 0.082 | 0.958 | 0.980 | 3.2776 | 0.942 | 0.012 | 1.161 | 0.957 |
| 3Years aged CBC $NO^{-}_{3}$-N | 4.705 | 0.115 | 0.962 | 1.348 | 3.827 | 0.985 | 0.493 | 1.165 | 0.989 |

### 4.3.4.4 $NH^{+}{}_{4}$-N adsorption kinetics on aged CBC

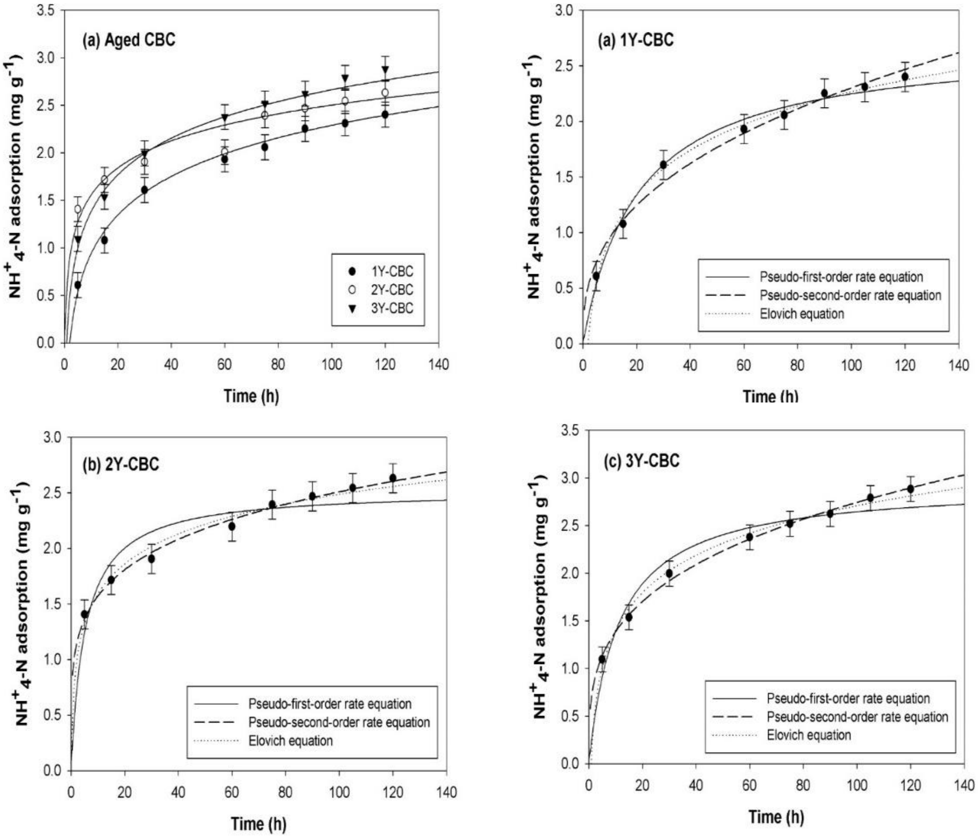


**Figure.4.13.** $NH_4^+$-N adsorption aged biochar for 1 year, 2 years and 3 years of CBC400.

We studied the adsorption kinetics of CBC biochars on NH4-N, as given in Table 4.9. and (Figure.4.12a), (Figure.4.12b), and found that it was better suited to a pseudo-second-order rate model as illustrated in (Figure 4.12 a), (Figure.4.12b), and (Figure.4.12c). Maximum adsorption was reached in 120 min. The two biochars sorbed the ammonium ($NH_4^+$ -N) in aqueous solutions in a short amount of time. While (Figure 8.a CBC), biochar the first year was slow release from biochar compared to 2 and 3 years. The three kinetics models with $R^2$ values greater than

0.871 were chosen to excite the experimental data (Table 4.9).

The pseudo-first order model might explain why, as adsorption capacity increases, the adsorption rate decreases linearly (Sahin et al., 2017). The rate-limiting interaction between two reagent particles, as well as the adsorption rate addressed by chemical adsorption processes such as electron sharing and electron transfer, is the rate-limiting factor, according to the pseudo-second order kinetic model (Ho et al., 2002). The Elovich model was developed to explain why CO molecules chemisorb in the first place (Zeldowitsch J. et al., 1934). As a consequence, the equation accurately explains the chemisorption of molecules, such as $NH_4^+$-N, in this case. The findings show that $NH_4^+$-N adsorption plays a major role in even monolayer ammonium adsorption, and that a pseudo-first-order rate equation (Zhang Wenliang et al., 2021) was utilized to calculate the rate. Aside from that, the CBC-$NH4^+$-N $q_e$ values have risen.

### 4.3.5.4 NO$_3$-N adsorption kinetics on 1$^{st}$, 2$^{nd}$, and 3$^{rd}$ year of Aged CBC

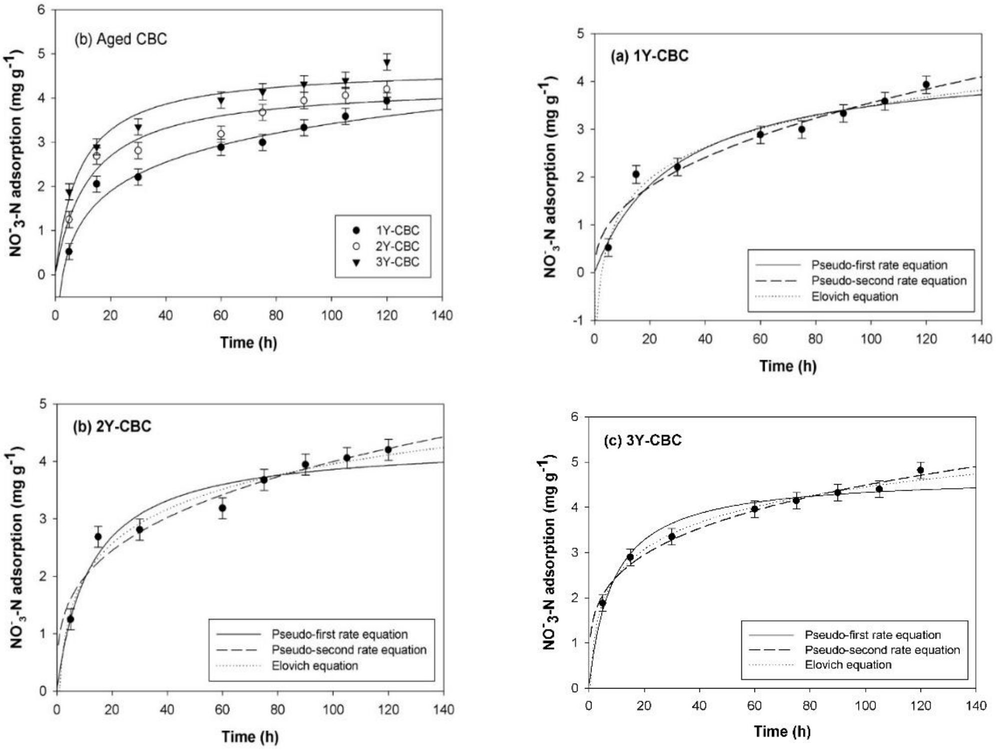
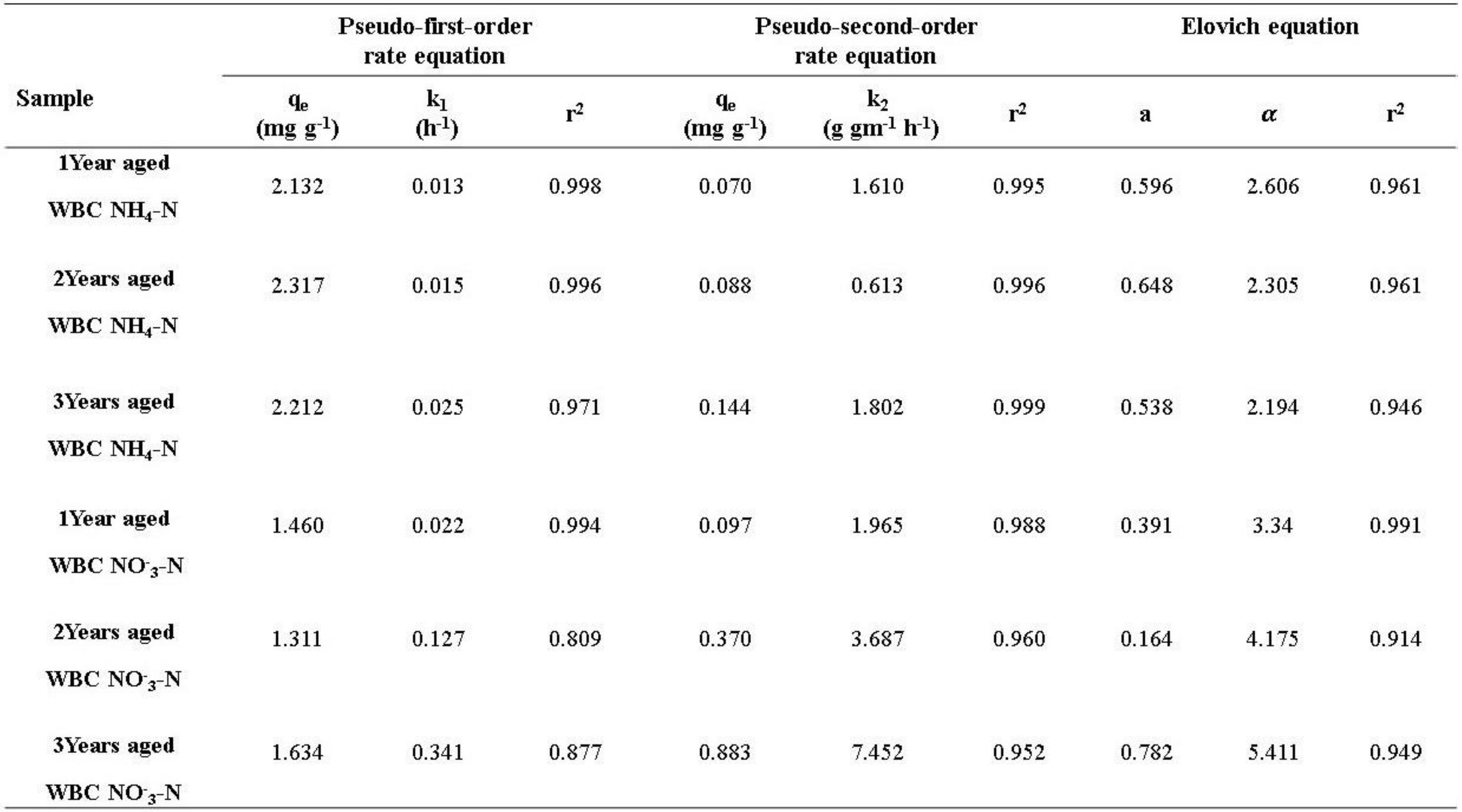


**Figure. 4. 13.** NO$_3^-$-N adsorption aged biochar for one, two and three year(s) of WBC.

NO$_3$-N adsorption kinetics on WBC surface, nearly matched date to the Elovich equation describes CO chemisorption, and the pseudo–second–rate equation revealed that aged biochar processing involves chemical adsorption processes into aqueous solution. The pseudo second order rate equation was shown to be incorrect due to physicochemical adsorption on aged biochar surfaces is preferable in (Figure.4.13).

**Table.4.12.** Parameters of adsorption kinetics models for adsorption of $NH_4^+$-N and $NO_3$-N onto Aged WBC of biochars



| Sample | Pseudo-first-order rate equation | | | Pseudo-second-order rate equation | | | Elovich equation | | |
|---|---|---|---|---|---|---|---|---|---|
| | $q_e$ (mg $g^{-1}$) | $k_1$ ($h^{-1}$) | $r^2$ | $q_e$ (mg $g^{-1}$) | $k_2$ (g $gm^{-1}$ $h^{-1}$) | $r^2$ | a | $\alpha$ | $r^2$ |
| 1Year aged WBC $NH_4$-N | 2.132 | 0.013 | 0.998 | 0.070 | 1.610 | 0.995 | 0.596 | 2.606 | 0.961 |
| 2Years aged WBC $NH_4$-N | 2.317 | 0.015 | 0.996 | 0.088 | 0.613 | 0.996 | 0.648 | 2.305 | 0.961 |
| 3Years aged WBC $NH_4$-N | 2.212 | 0.025 | 0.971 | 0.144 | 1.802 | 0.999 | 0.538 | 2.194 | 0.946 |
| 1Year aged WBC $NO^-_3$-N | 1.460 | 0.022 | 0.994 | 0.097 | 1.965 | 0.988 | 0.391 | 3.34 | 0.991 |
| 2Years aged WBC $NO^-_3$-N | 1.311 | 0.127 | 0.809 | 0.370 | 3.687 | 0.960 | 0.164 | 4.175 | 0.914 |
| 3Years aged WBC $NO^-_3$-N | 1.634 | 0.341 | 0.877 | 0.883 | 7.452 | 0.952 | 0.782 | 5.411 | 0.949 |

### 4.3.5. 5 $NH^+_4$-N and $NO_3$-N adsorption kinetics on aged CBC and WBC

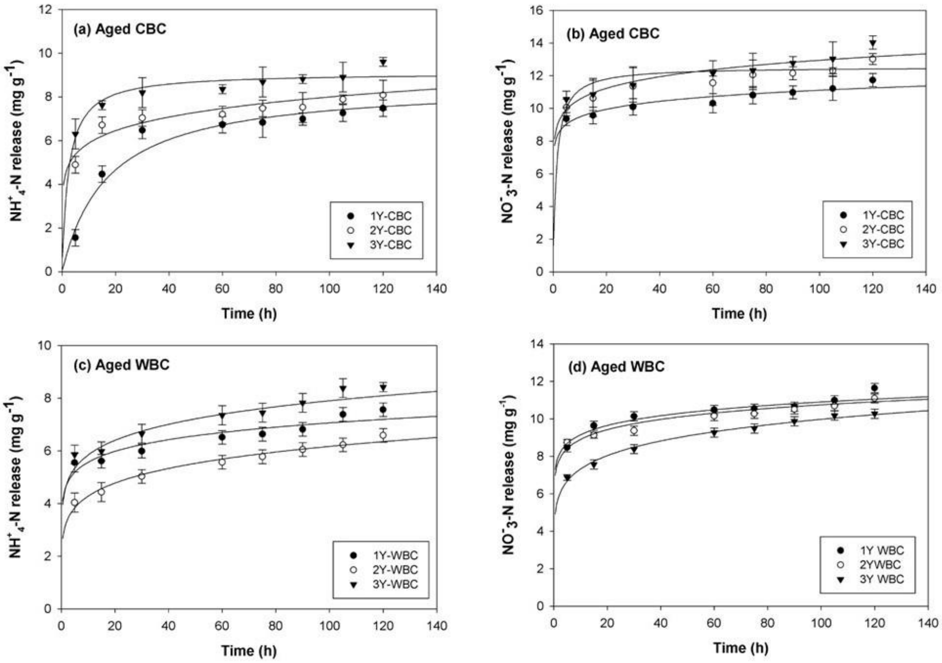


**Figure. 4.15** Comparative $NH_4$-N and $NO_3$-N release on aged CBC and aged WBC with different years

As (figure 13) shown that the only two years aged WBC was slower $NH_4$- N release from the two years aged WBC than one year and three years of aged WBC, because of the high dissolved organic carbon concentration (DOC), moreover the use of biochar to adsorb ammonia ($NH_3$) reduces $NH_3$ and $NO_3^-$ losses during composting and provides a method for the development of slow-release fertilizers. This result is significant for crop productivity because $NH_4^+$-N exchange permits biochars to absorb and release ammonium-nitrogen fertilizers via cation exchange.

### 4.3.5. 6 $NH^{+}{}_{4}$-N adsorption kinetics on aged CBC

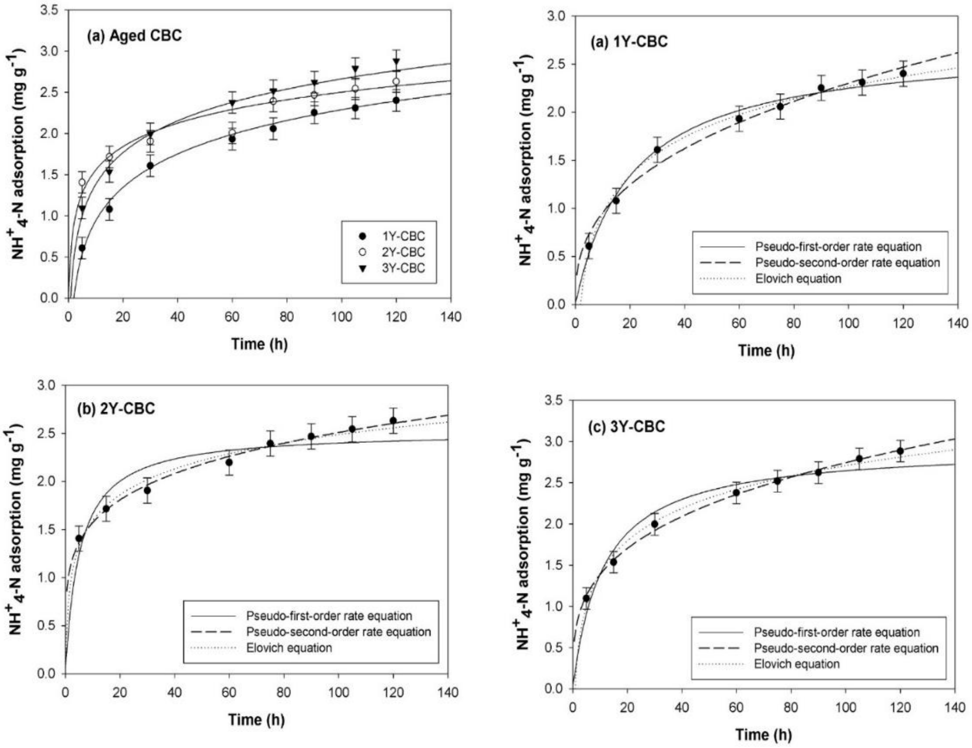


**Figure. 4.16.** Adsorption kinetics $NH_4$-N on aged CBC and aged WBC with different years

The sorption kinetics of ammonium on aged CBC and aged WBC are demonstrated in (Figure 4.15), (Figure 4.14) and Table 4.10 show the various parameters. The adsorption of chosen adsorbents to $NH_4^+$-N and $NO_3^-$-N achieved the apparent sorption equilibrium point after approximately 120 minutes, as shown in (Figure. 4.10). Both pseudo-first-order, pseudo-second-order (Lai Wei Yu et al., 2013), and elovich models fit the adsorption data well, as indicated by the regression coefficient ($R^2$). Ammonium adsorbed on aged WBC was significantly greater than that adsorbed on NO3-N WBC. As a treatment, three-year-aged biochars had a higher sorption rate ($k_2$) than first-year-aged WBC-$NH_4^+$-N (Table.4.10), and 3YWBC-$NO_3^-$-N had the highest $k_2$ (7.452 mg g$^{-1}$h$^{-1}$) of the five adsorbents. Additionally, the equilibrium point of adsorption would be reached after approximately 120 minutes in a 100 mg $L^{-1}$ $NH_4^+$-N and $NO_3^-$-N solution (Gai Xiapu et al., 2014). According to the fitting results, chemical interactions may be regulating the rapid sorption on the selected adsorbents. The previous researches (Wang, W. et al., 2019; Liu H. et al., 2012), intra particle diffusion was used to adjust the adsorption (Lai Wei Yu et al., 2013) velocity on granular porous adsorbents. Our results of (Figure. 4.10), we could have contributed to second order rate equation was fit better Elovich and first order models.

### 4.3.5. 7 $NO_3^-$-N adsorption kinetics on aged CBC

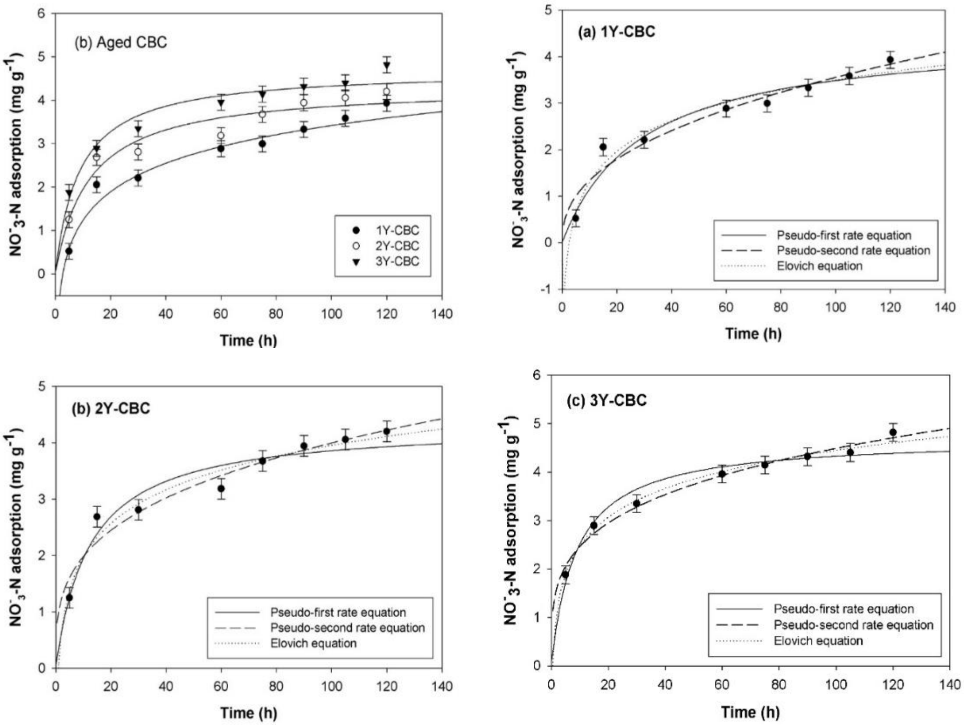


**Figure. 4.17.** Adsorption kinetics $NO_3^-$-N on aged CBC and aged WBC with different years.

Adsorption $NO_3^-$-N on aged CBC showed that one year aged of CBC was slow adsorption compared to two years and three years aged biochar in (Figure. 12b) aged CBC. The findings showed that the second order model was well fit in order to make the fitting data with three equations obvious. Figures 4.16a, 4.16b, and 4.16c of the CBC show isothermal and kinetic adsorption in pseudo-second-order models.

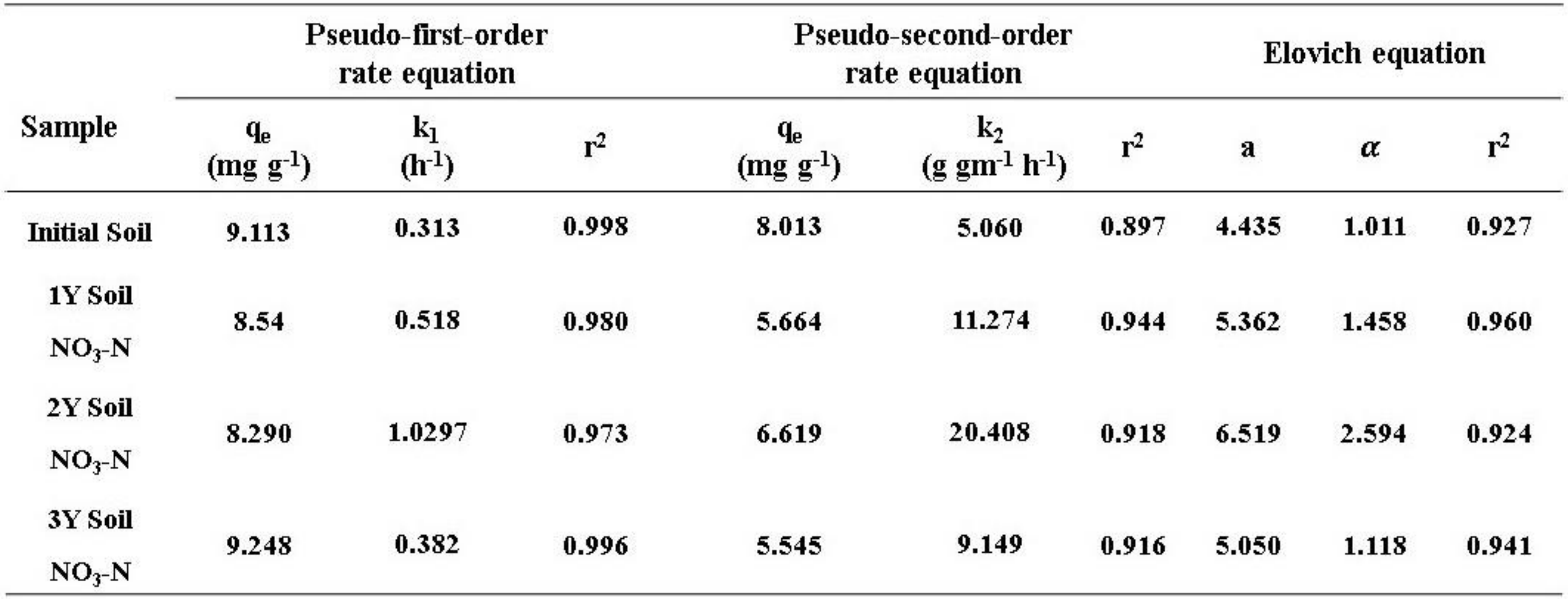
This contributes to the fact that adsorption is a physical-chemical process dominated by physical interactions. The physical adsorption is mainly owing to the mesoporous structure, specific surface area (Dai, Y. et al., 2020), Wang, Z. et al., 2020). Thus, the physical adsorption mainly comprises surface adsorption (relate adsorption, similar to gravitational interaction between the mass objects), intra particle diffusion, and electrostatic interaction for $NH_4^+$, and $NO_3^-$ adsorption on CBC and WBC biochars.

#### 4.3.5. 8 $NH_4^+$-N and $NO_3^-$-N Adsorption Kinetics onto three years of soil applications

Adsorption kinetics of $NO_3^-$-N onto soil ($NO_3^-$-N: 100 mg/L), 1Y-Soil, 2Y-Soil, and 3Y-Soil. We used 0.5 g aged soils with temperature 25˚C conduction and contact time was fixed 120 min for batch experiment. Soil depth (0 - >20 cm).

The parameters of adsorption kinetics models for $NO_3^-$-N adsorption (Park M. H. 2019) on soil surfaces are shown in Table 4.10. For the batch experiment, the contact time was set at 120 minutes.

**Table 4.13.** Parameters of adsorption kinetics models for adsorption of $NO_3^-$-N onto soil surface. The contact time was fixed 120 min for batch experiment



| Sample | Pseudo-first-order rate equation | | | Pseudo-second-order rate equation | | | Elovich equation | | |
|---|---|---|---|---|---|---|---|---|---|
| | $q_e$ (mg $g^{-1}$) | $k_1$ ($h^{-1}$) | $r^2$ | $q_e$ (mg $g^{-1}$) | $k_2$ (g $gm^{-1}$ $h^{-1}$) | $r^2$ | a | $\alpha$ | $r^2$ |
| Initial Soil | 9.113 | 0.313 | 0.998 | 8.013 | 5.060 | 0.897 | 4.435 | 1.011 | 0.927 |
| 1Y Soil $NO_3$-N | 8.54 | 0.518 | 0.980 | 5.664 | 11.274 | 0.944 | 5.362 | 1.458 | 0.960 |
| 2Y Soil $NO_3$-N | 8.290 | 1.0297 | 0.973 | 6.619 | 20.408 | 0.918 | 6.519 | 2.594 | 0.924 |
| 3Y Soil $NO_3$-N | 9.248 | 0.382 | 0.996 | 5.545 | 9.149 | 0.916 | 5.050 | 1.118 | 0.941 |

As results Table 4.11. shown that values $R^2 = 0.99$ and $q_e = 9.248$, this is indicating that first order was fit model first order due to molecule adsorption $NO_3^-$

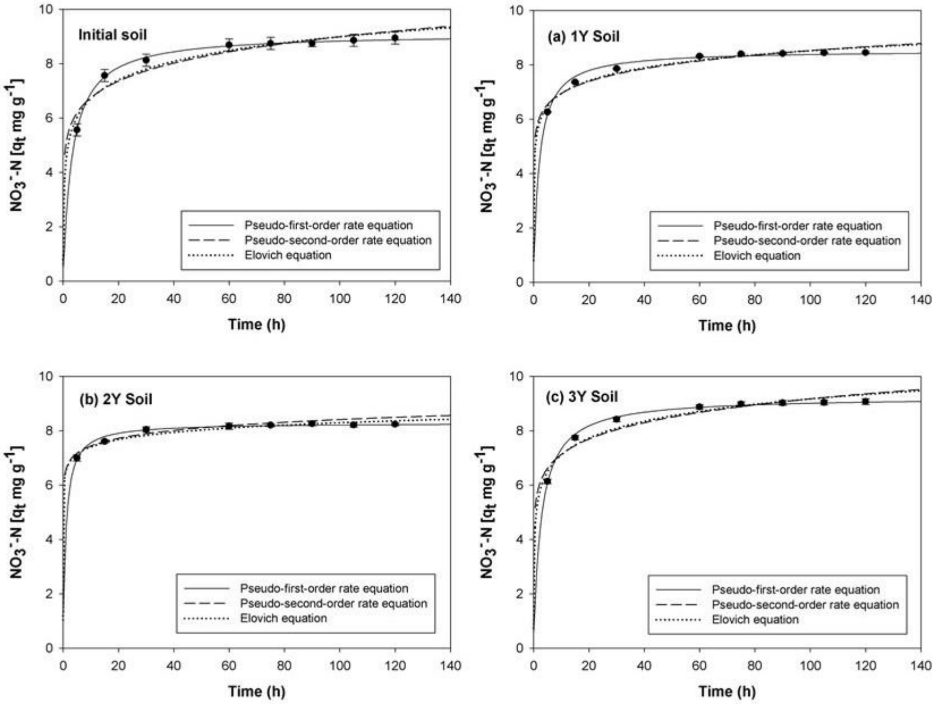


**Figure. 4.18.** Effect of contact time on $NO_3$-N adsorption for three types of soils from a batch experiment using soil for one year, soil for two years, and soil for three years' application.

The findings showed that maximal $NO_3^-$-N adsorption is affected by the initial $NO_3^-$-N concentration as well as soil components, particularly OM and clay content. Adsorption and binding of $NO_3^-$-N may include interactions with functional groups on the soil surface. More OM and positive charge of the oxides on NO3-N sorption may be found in deeper layers (60-90cm) and (90-120cm) (Hamdi W. et al., 2013).

### 4.3.5. 9 $NH_4$-N and $NO_3$-N Desorption Kinetics onto aged biochars of CBC and WBC

### 4.3.5 .9.1 $NH_4$-N and $NO_3$-Ndesorption kinetics on Aged CBC and WBC

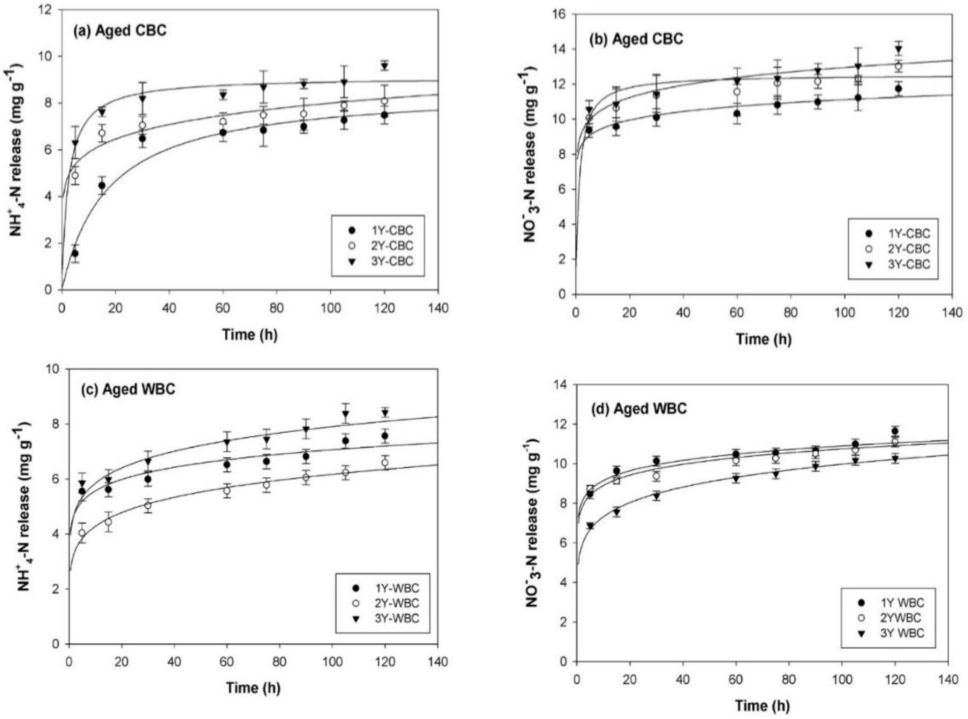
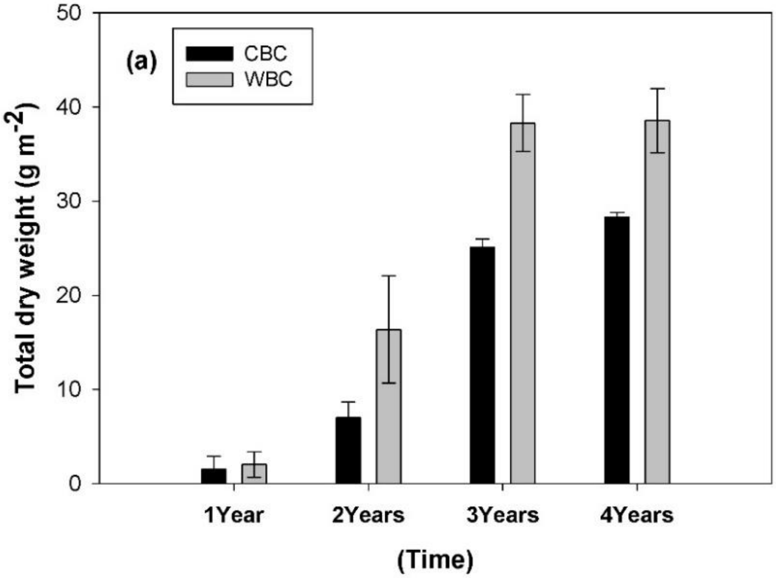


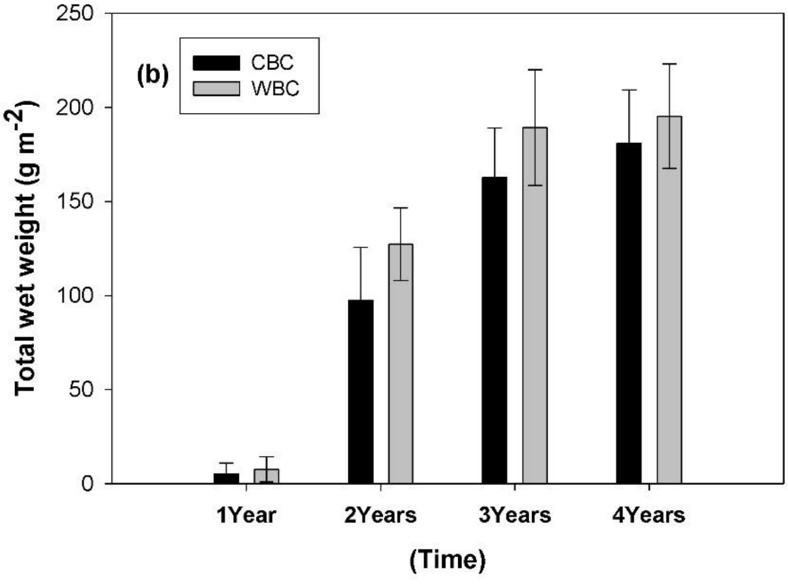
**Figure. 4.19.** Desorption kinetics $NH_4$-N and $NO_3$-N on aged CBC and aged WBC with different years.

As every first year of aged biochar were slow release N from biochar compare to two and three years of $NH_4^+$ and $NO_3^-$, respectively. However, $NH_4^-$ desorption onto two years aged WBC was slower than release of one and three years in (Figure. 4. 18c).

### 4.3.4.10. Effect of aged biochar on Pak Choi Growth

As the results show that CBC application for the first year was significant decreased by 1.54% to 0.59 % respectively was observed in (Figure. 15a). Similarly, dry weigh of WBC was significant decreased at dose of 5.0% compare to control of each year application. While dry weight for 3rd year of CBC and WBC were increased by14.01 % to 22.66% and 13.87% to 22.66 % respectively compared to control in (Figure. 17a), and (Figure. 17b).





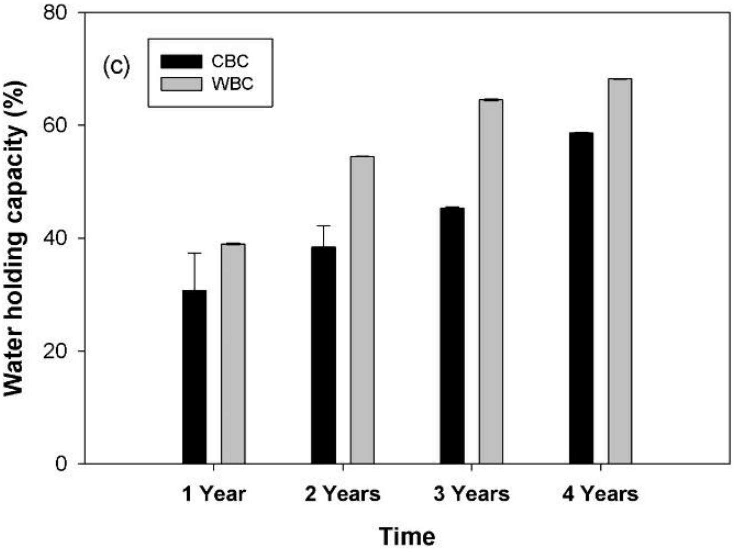


**Figure.4.20** Comparison of influent CBC and WBC application with different seasons (a) total dry weight, (b) total wet weight, and (C) WHC of soils.

It was observed that the different seasons as figure. 4.19 shown that water use efficiency will need to be substantially improved if we are going to use the sandy for agricultural purposes since these soils are excessively drained soils. In conclude aged CBC and WBC using in this experiment useful for application in plot filed test. Basso, et al., 2013, reported that this experiment has a water holding capacity of 57.61% when used CBC at 5.0% at 4 years that is enhanced by the pyrolysis process. The resulting in 64.92% in water retention in WBC, dose of 5.0% by weight.

## 4.4. Summary

Through use of CBC did not indicate a significant difference in ageing BC in the second year ($p > 0.05$), but there was a notable difference in CBC in the third year ($p$ 0.05) when compared to the first year. When all treatments were compared to the control over the course of a year, there was a substantial difference in soil-mixture. WBC revealed a significant difference in dosages biochar application in treatments, with a $p < 0.05$ significance level. This is due to the active functional groups in soil media was not dissociated in deionized water condition. The elevated pH observed in this experiment could be due to an increase in soil pH caused by a single application of biochar. The higher pH of CBC, WBC 9.32, and 8.47 was most likely related to ash accumulation during treated soil. Carbonates alkali and alkali earth metals predominate in ash content. As a result, biochar application can enhance soil quality by raising the pH of the soil. To increase the pH of acidic soils, biochars might be used instead of lime materials.

The quantity of exchangeable cations and nutritional elements (e.g., Ca, K, Mg, and Na) may be enhanced following biochar application, which could improve the cation exchange capacity (CEC) and the availability of nutrients in (Figure.4.9) the result showed that Ca and K was increased for every year of soils-mixed CBC by 912 to 9.2 mg $g^{-1}$ compared to control while Mg and Na was slightly increased by 2.13 to 2.42 mg $g^{-}$ and 1.6 to 1.66 mg $g^{-1}$ respectively in (Figure.4.9a) and (Figure.4.9b) was increase Ca, and K by 8.51 to 9.10 mg $g^{-}$ and 7.32 to 8.52 gm $g^{-1}$ respectively. However, Mg and Na was not increased 2.18 to 2.77 mg $g^{-}$ and 0.30 to 1.120 mg $g^{-1}$. For the third year of soil-incorporated with CBC was increased Ca, and K from 8.74 to 9.89 mg $g^{-1}$ and 7.55 to 8.83 mg $g^{-1}$, respectively.

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# CHATPER 5

# INVESTIGATION OF THE PROPERTY CHANGE OF BIOCHAR AND MICROBIOLOGY UNDER LONG-TERM EXPOSURE IN SOIL AND UNDER PLOT CONDITION

## 5.1. Introduction

Biochar is a rich carbonaceous solid substance produced by pyrolyzing agricultural and woody residual biomass at temperatures ranging from 300 to 1000 degrees Celsius in oxygen-limited or oxygen-free environments. It possesses a high pH, a porous structure, a wide surface area, and a microporous volume, as well as greater heat stability and adsorption capability ( Zwieten., 2010). Because the quality of biochar varies depending on the feedstock and/or pyrolysis conditions, soil physical and hydraulic properties such as air exposure, combustion duration, and temperature should be impacted differently (Lehmann et al., 2002). It was introduced as a soil supplement to offer long-term carbon enrichment while improving water retention (Safan et al., 2020); macro- and micronutrient retention; and soil microbial activity (Pokharel et al., 2020), which can also assist in nitrogen fixation (Pokharel et al., 2020). Soil porosity, water holding capacity, pH, and nutrient retention are all improved by biochar. Biochar is well-known for its excellent sorption and adsorption properties, and it is frequently utilized for heavy metal ion removal (Saleem J. et al., 2019). Coffee grounds (CBC) and woodchips (WBC) were not tested after being pyrolyzed at 400 °C for 2 hours.

The effects of biochar on the organization of soil microbial community structure (Aghoghovwia, M. P., 2018) are complicated and vary, and various soil microbial communities' (Laetitia Herrmann, et al., 2019) reactions differed following biochar application (Khodadad et al., 2011; Laetitia Herrmann, et al., 2019). To achieve large agricultural yields, good soil conditions are necessary. As a result, it's critical to research and use soil amendments. Biochar is fundamentally stable, nutrient-dense, and may last for thousands of years in soil (Ouyang et al., 2013; Amin et al., 2016). Furthermore, biocahr is regarded as a beneficial soil amendment due to its numerous soil health advantages. Long-term application of woodchip biochar substantially enhanced microbial communities and surface, according to (Espinosa N.J et al., 2020). Coffee biochars enhance bacterial diversity and fungus, as well as the quantity of Escherichia coli and Salmonella ssp., according to (Pepper, I.L., et al., 2005). Rice straw biochar is added to tomato growing grounds to boost root biomass and DNA concentration. The impact of CBC and WBC on DNA and mRNA concentrations, on the other hand, has not been well investigated.

The goal of this study, as described in this chapter, was to assess the influence of CBC and WBC on soil nutrients and microbial community structure, with the results potentially providing theoretical and practical direction for long-term biochar application.

## 5.2. Materials and Methods

### 5.2.1. Experimental design and sampling

Sand loamy soils were collected from each plot test before planting and after harvested. The soils samples were storage under 5 ˚C a week in refrigerator for adsorption and desorption test, pH and moisture content. However, soils samples for analysis of microbial community store under below -12 degree Celsius. Due to soil samples for adsorption and desorption were ground 2 mm sieve and dry 105 ˚C for 48 h.

### 5.2.2. Biochar production and properties

Biochars were produced from two common feedstock: coffee ground and wood chips. Raw materials were collected from coffee shop and garden woodchip at Seoul National University (SNU). Before pyrolysis, the woodchips were chopped into small (2 cm) pieces and oven-dried for two days (48 hours) at 105 °C. Under oxygen-limited circumstances, a biomass paralyzing furnace was utilized to convert the dry feedstock into biochar (TH-01, Germany). The pyrolysis temperature was raised to 400°C and held for 2 hours. The heating rate was increased every 5 °C/min before reaching the constant temperature. After the pyrolysis process, biochar yields were measured and grinded to pass through aluminum a 2 mm sieve.

### 5.2.3. Physiochemical properties of CBC400 and WBC400

Biochars were measured in a 1:20 ratio of biochar to deionized water and then shaking for one hour at room temperature at 25 °C with 60 rpm. The pH meter was calibrated with pH 7 and pH 10 buffers. After shaking and equilibration for 1 hour, the pH of the reference biochar in 0.01 M $CaCl_2$ with a biochar to $CaCl_2$ ratio of 1:20 was measured, and the final pH was recorded by Orion star A216.

Ash, moisture, and volatile matter content of biochars and soil were performed based on ASTM standard method. The fixed carbon content was calculated by differentiation.

The yield of biochars was calculated as follow:

$$\text{Yield (\%)} = [100 \times (\text{biochar mass} \div 105\ ^\circ\text{C dried biomas})] \qquad (1)$$

The substance that loses mass as a result is volatile (VM). For 6 hours, the biochars were cooked at 550°C in an open crucible. Ash content refers to the amount of materials left after burning. The following equation was used to calculate the concentration of fixed carbon (FC):

$$\text{FC (\%)} = [100 - (\text{VM} + \text{Ash})] \qquad (2)$$

### 5.2.4. Analysis of Soils

After shaken for 1 hour at room temperature at 25 °C at 60 rpm on a reciprocating shaker, the pH of the soil was determined in a 1:5 ratio of dirt to deionized water. The pH meter was calibrated using pH 7 and pH 10 buffers. After shaking and equilibration for 1h, the pH of the soil samples was measured in 0.01 M $CaCl_2$ with a soil to $CaCl_2$ ratio of 1:10, and the final pH was recorded by Orion star A216.

Dry combustion using a CHNS analyzer was used to evaluate the elemental compositions of biomass and biochars, including C, H, N, and S. (EA). In a nutshell, 1.0 g of samples were crushed to pass through a 2 mm sieve and then fed into a high-temperature (1,000°C) furnace where they were combusted in pure oxygen under static circumstances. Carbon was transformed to carbon dioxide, hydrogen to water, nitrogen to nitrogen gas/oxygen oxides, and sulphur to sulphur dioxide during combustion (Akoji Jibrin Noach et al., 2019). The gases were then passed through absorbent traps, resulting in just carbon dioxide, water, nitrogen, and sulphur dioxide (Akoji Jibrin Noach et al., 2019) remaining, which were then detected and recorded. Each element's weight % was determined.

$$O\ (\%) = [\ 100 - (C + H + N + S + Ash)] \qquad (3)$$

H/C, O/C, and (O+N)/C molecular ratios of biochars were determined using (Chen B. et al., 2008).

### 5.2.5. Extraction of Extraction of genomic DNA and mRNA (or DNA extraction and sequencing)

Using the primer pairs 341F (5´-CCTA CGGGNGGCWGCAG-3´)/785R (5´ -GACTACHVGGGTATCTAATCC-3´) and ITS1FC-3´) and the MP116004-500 Fast DNA spin kit for soil (MP Biomedical, Santa Anna, CA), DNA was extracted from 0.5 g of soils according to fragments of the V4 variable region of the 16S rRNA gene and the ITS region were amplified (Aghoghovwia M. P. 2018) forward primers for the bacterial and fungal populations, respectively, were barcoded. All the samples were mixed in equal DNA concentrations and purified with calibrated Ampure XP beads (Herrmann L. et al., 2019). The DNA library was created using purified DNA and followed the Illumina TruSeq DNA library preparation process. (https://www.ezbiocloud.net/Chunlab, South Korea) performed the sequencing.

### 5.2.5. Statistical Analysis

All data is presented as averages with standard deviations (SD) from at least three different replicates. IBM SPSS (Version 25.0) was used to conduct the statistical analysis. One-way analysis of variance (ANOVA) was used to determine the difference between treatments, with Duncan's multiple range test deeming p 0.05 significant. Sigmaplot 10.0 software was used to produce the graphics.

## 5.3 Results and discussion

### 5.3.1. Soil chemical attribute

The soil samples' physicochemical properties were examined, with the findings shown in Table 1.

**Table 5.12.** Physicochemical properties of the initial soil collected at SNU loop top of plot experiment.

| **Characteristics** | **Soil (initial soil)** |
|---|---|
| Bulk density (g $cm^3$) | 1.38 |
| pH (1:5) | 6.55 |
| Total soil organic carbon (g $kg^{-1}$) | 51.32 |
| Total nitrogen (g $kg^{-1}$) | 3.69 |
| Pore volume ($cm^3$ $g^{-1}$) | 0.21 |
| C/N ratio | 13.82 |
| CEC ($cmol_c$ $kg^{-1}$) | 14.25 |
| Water holding capacity (% by wet. Wt.) | 48.02 |
| Water filter pore space (%) | 43.59 |

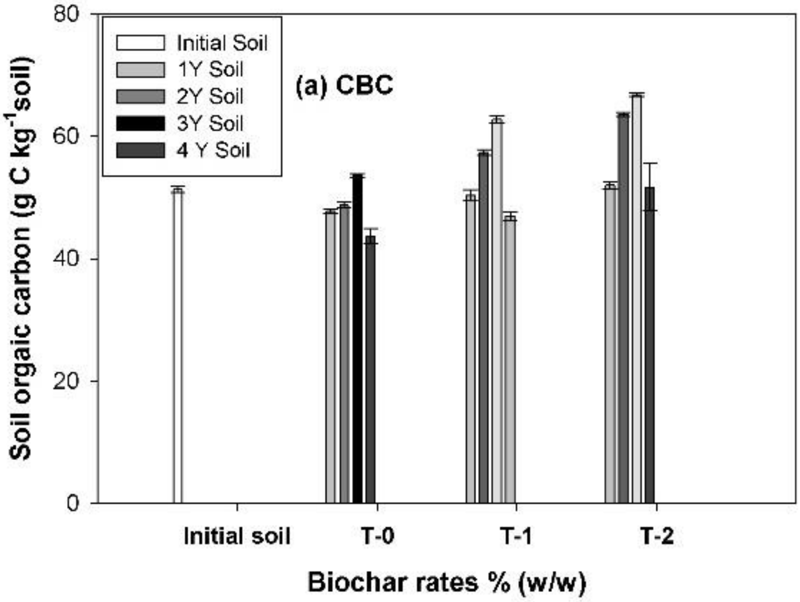
The physiochemical properties of the initial soil sample were analyzed as shown in Table 9. The average pH of soil sample was 6.55. The range of soil pH in this study was appropriated for vegetable (E.J. Penas, and D.T. Lindgren., 1990). Soil bulk density (1.38 g $cm^3$) is in the suitable range for plant growth. Carbon (20.7

g kg$^{-1}$) and nitrogen (1.5 g kg$^{-1}$) contents and CEC were considered as medium levels. C/N ratio of the initial soil was also in a normal range and similar to other cultivated soils. Water holding capacity and water filter pore space were also in a proper range.

### 5.3.2. Effects of Coffee ground and woodchip biochar on soil organic carbon(SOC) content, total nitrogen (TN), and C:N ratio.

#### 5.3.2.1. Total soil organic carbon (SOC)

The total soil organic carbon application on nitrogen and soils enhanced the mean values of soil organic carbon in (Figure.18a), and (Figure 18b).



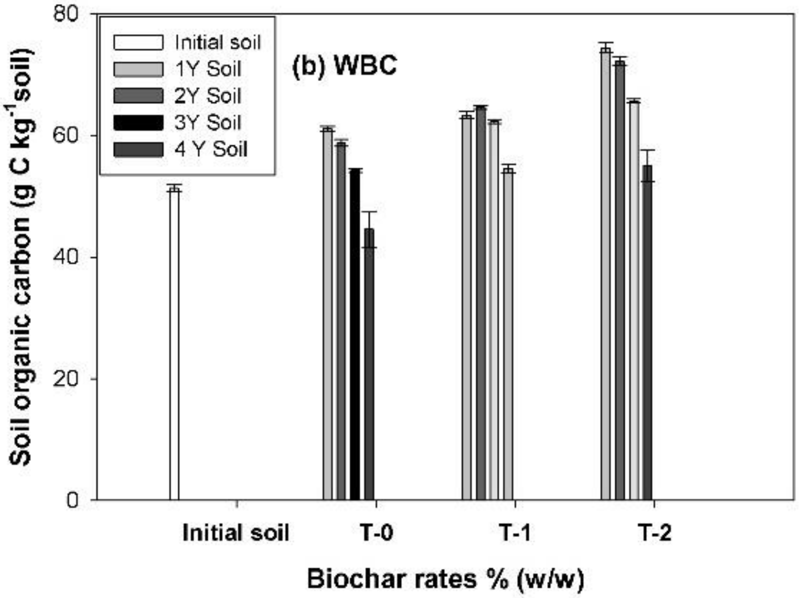


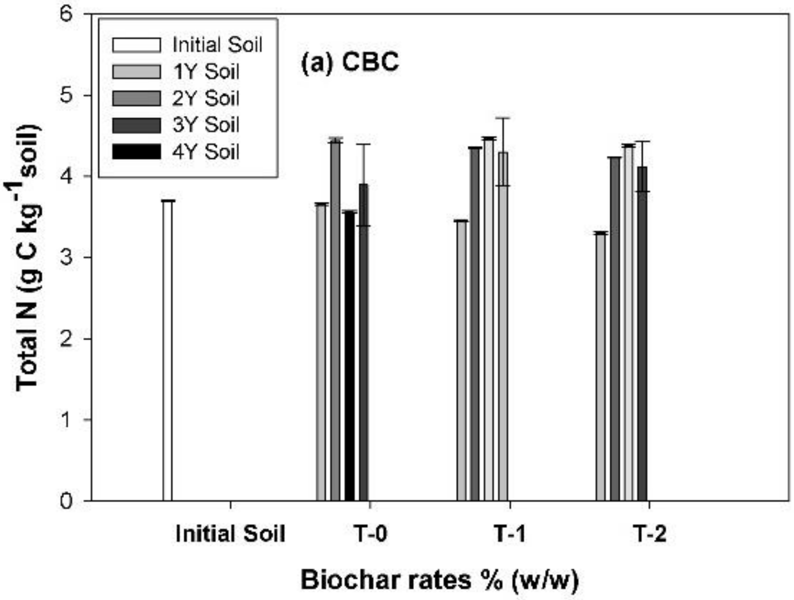
**Figure. 5.20.** Effect of (a) CBC, (b) WBC biochar application rate on soil organic carbon (SOC).

* Initial soil is the soil before planting, T-0-1, T-0-2, and T-0-3 is treatment without biochar in first year, second year, third year, and fourth year as confirmation. Treatment T-1-1, T-1-2, and T-1-3 are the designations for 1 (2.5 percent (w/w) of dose biochar in the first, second, and third years. T-2-1, T-2-2, and T-2-3 are treatments 2 (5.0 percent (w/w) of dose biochar in the first, second, third, and fourth years as confirmation, respectively.

The results shown that highest values of SOC were observed in soils amendedwith2.5%, and 5.0% (w/w) CBC respectively. The presence of significant amounts of carbon in the CBC and WBC might explain the increase in organic carbon caused by the addition of biochar. The greatest organic carbon levels in biochar-treated soils show biochar's recalcitrance. (Lehmann, 2007; Solomon et al., 2007; and Liang et al., 2006) also discovered that the ancient terra preta had greater organic C and total N than surrounding soils.

### 5.3.2.2. Total Nitrogen (TN)

The substantial effects of biochar amendment on soil total N at observed soil depths are described in this paper (Figure. 19).



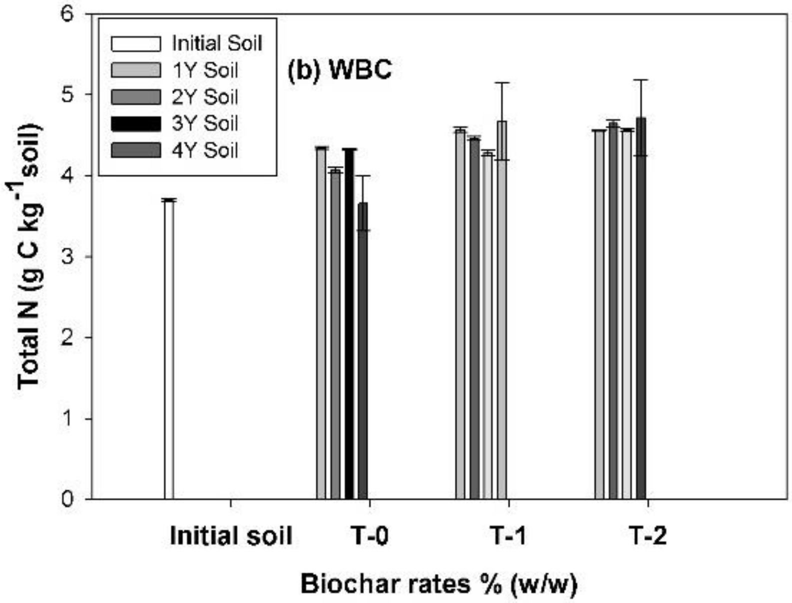
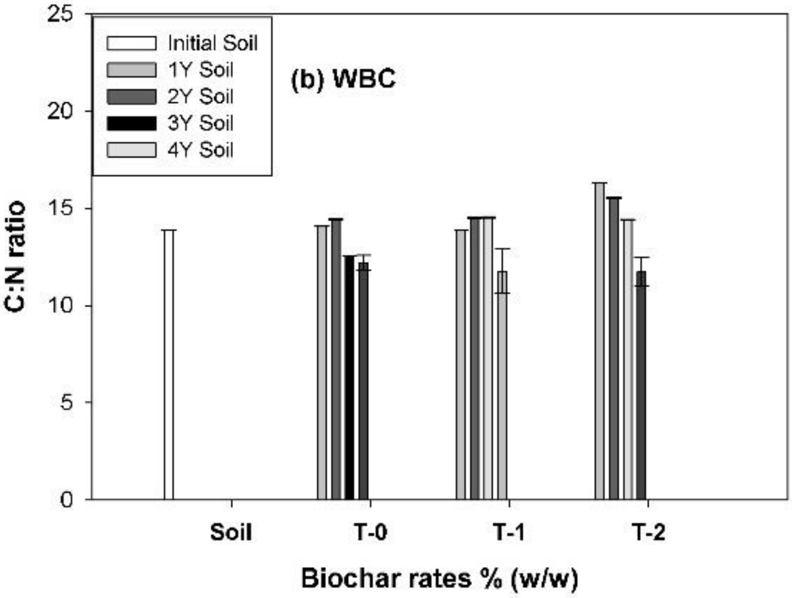


**Figure. 5.22.** The effect of added biochars on total nitrogen (TN) content in soil under (a) CBC and (b) WBC conditions.

As results showed that when compared to control and starting soil, adding biochar enhanced soil total N in all CBC and WBC treatments. Most investigations found that biochar amendment had no significant effect on soil total N leaching and desorption (Zhang Yaling et al., 2017). Biochar has the potential to absorb $NO_3^-$ or $NH_4^+$, reducing soil N leaching and increasing soil N retention (Zhang Yaling et al., 2017). Although it has been claimed that biochar's adsorption of NH4+ and NO3 is short-lived (Kameyamaet al., 2012; Zhang Yaling et al., 2017), substantial NO3 adsorption by biochar has been observed to occur over a year (Zhang Yaling et al., 2017). As a result, in this investigation, biochar adsorption of or $NH_4^+$-N or $NO_3^-$-N might be a possible method for improving soil N retention.

#### 5.3.2.3 Soil Carbon/ Nitrogen (C/N) ratio



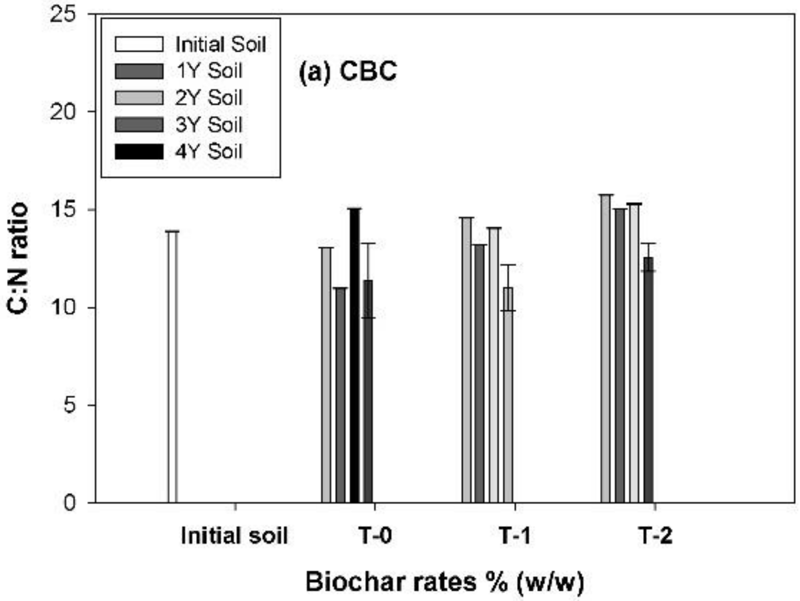


**Figure.5.23.** Response of biochar rate (a) CBC, and (b) WBC on C/N ratio

The significance of the C/N ratio as an indication of organic matter decomposability in forest soil was evaluated. The evaluation was based on the link between the C/N ratio and the concentrations of soil organic carbon (SOC), soil nitrogen, and soil organic carbon (SOC) (Total N). The mean SOC content in the WBC lot experiment site was higher than the CBC lot test, but the SOC content in the CBC lot test was lower (Figure.5.22b). The species in organic matter and their breakdown are connected to the SOC content. In the third year, the mean total N in the horizon soil in the CBC and WBC locations was identical, but there was more variety in the soil-mixture WBC. As a result, a high SOC content and equivalent total N content were shared by the greater C/N ratio in the lot experiment WBC compared to the lot test of CBC-mixed soil.

### 5.3.3. Biochar production

#### 5.3.3.1 Physiochemical properties of CBC and WBC

As shown in (Table 5.12), we have observed general dependent pH of the initial CBC and WBC. WBC400 and CBC400 had pH ranged from moderately alkaline (pH 8.47) to alkaline (pH 9.32), respectively. CBC400 had pH greater than WBC400 was applied. The high quantity of inorganic soluble salts corresponds to the biocahrs' basic pH. These findings are in accord with previous research that revealed biochar to be alkaline (Singh et al., 2010; Aghoghovwia M.P., 2018). The use of alkaline biochar to amend acidic soil has a liming effect (Aghoghovwia M.P., 2018). However, when alkaline biochars are put to neutral or alkaline soils, they cause a slew of problems. A soil pH of greater than 8 may, for example, have a negative impact on plant growth and deplete available P as well as some minerals (Artiola et al., 2012). Proton activity was minimal in the alkaline biochar because surface charge and exchangeable acidity are both a function of pH, implying that the displacement of protons from hydration fluids was favored (Aghoghovwia M.P., 2018).

Both biochars generated similar yields under similar pyrolysis temperatures and times, ranging from 32.49 percent for CBC to 33.93 percent for WBC (Table 1). The black C proportion in biochars is represented by the fixed C content, which is used to determine the lifetime of biochars in soil. The non-combustible mineral fraction of biochars is referred to by the percentage of ash, whereas the non-combustible mineral fraction of biochars is referred to by the percentage of ash (Enders et al., 2012). Although the ash content of CBC (2.9 percent) was lower than that of WBC (11.6 percent), it was higher than that of coffee residue (CR) 0.73 percent and 1.7 percent (Tsai et al., 2012; Naruephat T. 2019) Many studies have demonstrated that biochars with a high ash concentration are rich in nutrients and have a high alkalizing capability (Tsai et al., 2012; Naruephat T. 2019). (Deenik JL et al., 2011). Although CBC had low ash, it was high fixed C (81.25%) as compared to WBC (67.63%) and both of which had fixed C above 50% and low volatiles matters, indicating good potential for carbon sequestration.

Biochars in this study had high C and low N which brought about high C/N ratio, ranging from about 52 for CBC and 312 for WCB, respectively. When applied to soils, a broad C/N ratio higher than 30:1 has negative consequences that might lead to net N immobilization (Havlin, 2014). Due to nutrient nitrogen immobilization process, all of the biochars examined may potentially reduce mineral N.

WBC and CBC of the O/C and H/C ratios were comparable, ranging from 0.17 to 0.61 percent and 0.59 percent to 0.86 percent, respectively (table 2). The H/C ratio should have a maximum threshold value of 0.7 (Aghoghovwia M.P., 2018), according to the IBI 2015, and the O/C ratio should have a maximum threshold value of 0.4, according to the EBC- 2012. The biochars have less carbonization, aromaticity (H/C), and polarity (O/C) (Aghoghovwia M.P., 2018) when the atomic ratios of the components are higher. It's worth noting that the O/C and H/C ratios in this study's biochars were near to the recommended thresholds, suggesting that biochars had low oxygen and high C and were therefore classified as well-pyrolyzed ranges with aromatic structure enrichment, prone to degradation, and stable properties (Masiello., 2004). The O/C and H/C ratios in (Chhabra P. S. et al., 2009) WBC were lower than in CBC. This implies that WBC has more aromatic compounds and is more stable, whereas CBC contains greater chemical reactivity and has a less hydrophilic surface. Both biochars, however, had a comparable water holding capacity of about 27.4%.

The CBC and WBC's specific surface area, pore volume, and pore size are also listed (Table 5.14). Biochars' surface area indicates how effective their surface shape is in adsorbing different solutes (Lehmann et al., 2006). The structural change in biochar particles following heat treatment was shown by the pore architectures of biochars, which was a crucial characteristic for sorbent materials.

**Table 5.14.** The physicochemical properties of coffee ground (CBC) and Woodchip (WBC) biochars pyrolyzed at 400 °C for 2 h.

| **Characteristics** | | **Biochar** | | **Aromaticity criteria** |
|---|---|---|---|---|
| | | **Coffee ground** | **Woodchip** | |
| Yield (%) | | 32.49 | 33.93 | |
| pH | | 9.32 | 9.83 | |
| Proximate analysis (wt.%, dry-basis) | Fixed carbon | 81.25 | 67.63 | |
| | Volatile matter | 15.85 | 20.77 | |
| | Ash | 2.9 | 11.60 | |
| Ultimate analysis (wt.%, dry basis) | C | 52.45 | 78.0 | |
| | H | 3.7 | 3.84 | |
| | N | 1.0 | 0.25 | |
| | O | 42.85 | 17.91 | |
| | H to C | 0.85 | 0.59 | < 0.6 |
| | O to C | 0.61 | 0.17 | < 1.7 |
| Elemental composition (g/kg) | K | 19.16 | 4.82 | |
| | Ca | 1.74 | 7.87 | |
| | Mg | 1.04 | 1.06 | |
| | Na | 1.15 | 8.86 | |
| Surface area (m2/g) | | 0.44 | 2.91 | |
| Pore volume (cm3/g) | | 0.011 | 0.011 | |
| Mean pore diameter (nm) | | 98.28 | 14.92 | |
| CEC (cmol/kg) | | 29.67 | 31.44 | |
| WHC (% by wet wt.) | | 27.4 ± 4.9 | 27.4 ± 4.9 | |

WBC had higher surface area (2.91 m² $g^{-1}$) than CBC (0.44 m² $g^{-1}$), indicating that WBC might be good for nutrient adsorption than CBC, however, both of which had low surface area. The low surface area might have related to the pyrolytic temperature (Joseph et al., 2009) and the processes of softening, melting, fusion, and carbonization during pyrolysis (Fu et al., 2011). These mechanisms block gas adsorption in the pores, resulting in small surface areas. The presence of compositional components (lignin, cellulose, and hemicellulose) in feedstock contributes to the large surface area of WBC (Kizito et al., 2019The pore volume of CBC and WBC was similar, however the mean pore sizes were different. The mean pore diameter of CBC (98.98 nm) was larger than that of WBC (14.92 nm).

CEC is a significant source of biochars in soil, and it plays an essential role in nutrient adsorption and desorption, as well as nutrient retention (Glaser et al., 2001). Biochar CEC is very variable, ranging from 5 to 50 cmol kg1 and even reaching 69 to 204 cmol kg1 (Echeverri et al., 2018). A study comparing maize stover biochar pyrolyzed at 450°C and 700 °C found that the lower temperature produced biochar with a CEC twice as high as the high pyrolytic (Aghoghovwia, M. P. 2018), leading to the conclusion that applying lower pyrolytic biochar to soil can improve soil CEC and contribute to C sequestration (Aghoghovwia, M. P. 2018). The CEC of biochars was comparable and ranged from around 29.67 cmol $kg^{-1}$ to 31.44 cmol $kg^{-1}$. The original soil's CEC was in the average range, indicating that it was appropriate for holding and exchanging cations in the soil solution.

### 5.3.2.2 Biochar Surface Area and Pore Volume

**Table 5.14. Surface area and pore volumes of CBC and WBC pyrolysed at 400°C for 2h.**

| Sample | BET Surface Area | Micropore Volume | Total Pore Volume | Average Pore Diameter |
|---|---|---|---|---|
| | (m$^2$ g$^{-1}$) | (cm$^3$. g$^{-1}$) | (cm$^3$. g$^{-1}$) | (nm) |
| CBC400 | 0.4378 | 0.1006 | 0.0107 | 98.2810 |
| WBC400 | 2.9061 | 0.6677 | 0.0108 | 14.9240 |

Biochar's BET specific surface area indicates how effective its surface shape is in adsorbing different solutes (Table 5.14). The BET surface area of WBC400 was higher than that of CBC400. Feedstocks and pyrolyzed temperature may explain the differences in BET surface area between CBC400 and WBC400. (Shohi et al., 2010) discovered that different feedstocks result in variable amounts of surcase area, pores, and functional groups in biochars, all of which affect biochar sorption properties (Gai Xiapu et al., 2014). The low BET specific surface area of CBC400 and WBC400 biochars (Aghoghovwia Makhosazana P. et al., 2020) could be due to high amounts of inorganic alkaline species, which can impede access to biochar micropores, reducing surface area (Aghoghovwia M. P., 2018).

### **5.3.3.** Bacterial and fungal sequencing data

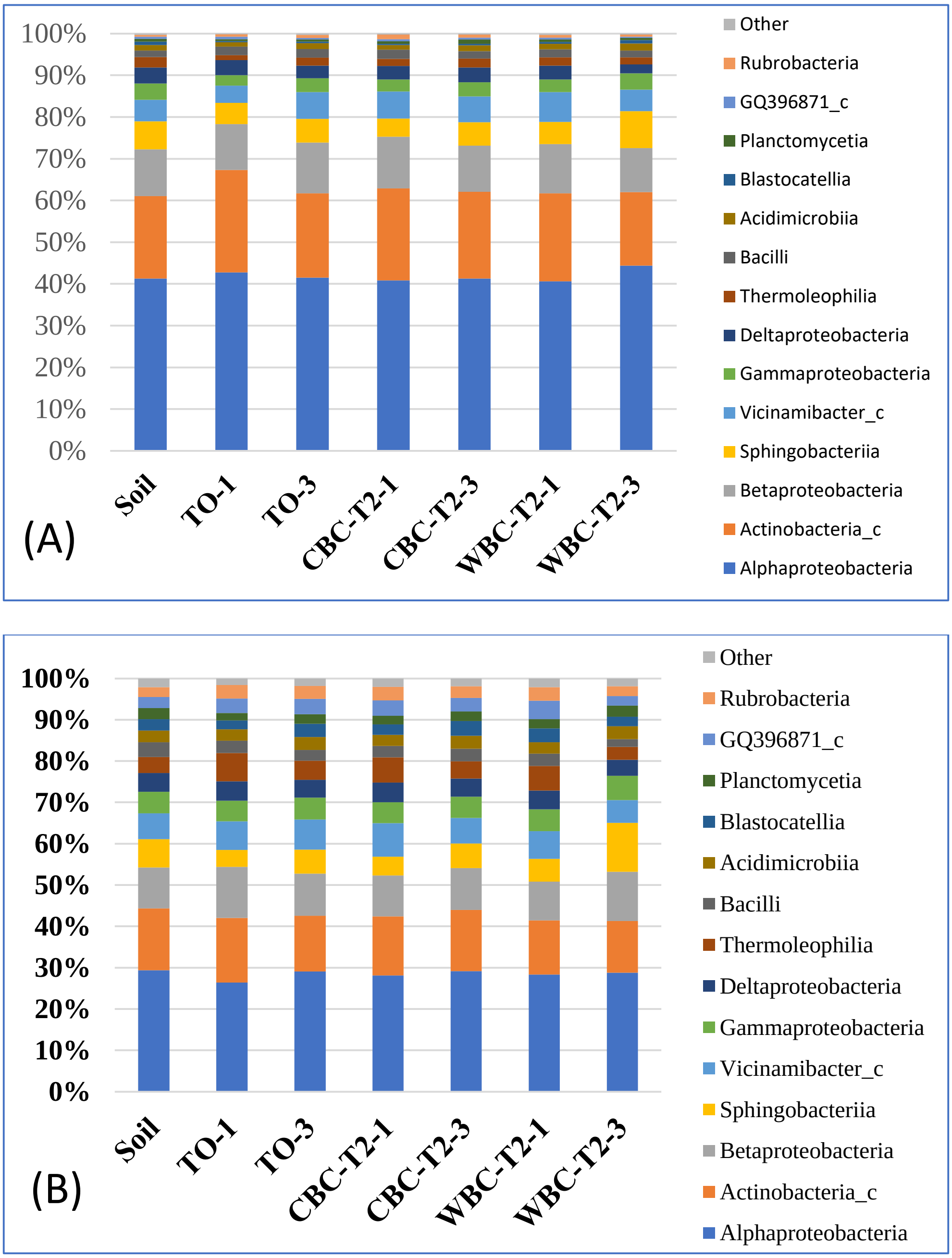


**Figure.5.24**. The phylum (A) and class (B) composition of the soil bacterial population in the bacterial and fungal samples were preserved databases under

different treatments, with 3,401,226 and 4,490,456 quality filtered readings, respectively. Bacterial sequences were classified into 32,742 OTU, organized into 239 families and 29 phyla, whereas fungal sequences were divided into 10,709 OTU, organized into 562 families and 31 phyla.

As the (Figure 5.23 A and B), in practice, the application of biochar (CBC-400, WBC-400) in the plot experiment with different doses of biochar at 2.5%, and 5.0% (w/w) has not changed the microbial community in the last three and four years, which is confirmed. Therefore, we can add any fertilizer along with biochar application in the future research.

### 5.3.4. Composition, richness, and diversity of the bacterial community

In all biochar dose-soil class combinations (Hermann L. et al., 2019), Proteobacteria (>40 percent) dominated the bacterial population, followed by Actinobacteria (>20 percent), Acidobacteria (>12 percent), and Firmicutes (>8 percent). Alphaproteobacteria (>24 percent), Actinobacteria (>13 percent), Betaproteobacteria (>10 percent), and Sphingobacteria (>10 percent) were the most common classes. The bulk of the bacterial phyla and classes discovered in the different samples (Hermann L. et al., 2019) were impacted by the soil class, regardless of the biochar dose (Aghoghovwia, M. P. 2018) (8 out of 9 phyla and 12 out of 15 classes). When soil classes were studied separately, however, biochar treatment had a moderate and variable effect on the abundance of the major phyla and classes (Aghoghovwia, M. P. 2018) (Figure. 5.23A, B). Planctomycetes reduced in soils after charcoal application (P = 0.027), whereas Gemmatimonadetes increased (*P* = 0.036). Acidobacteria abundance dropped considerably in WBC soils following application of biochar doses more than 5.0 percent by weight ($P = 0.003$), whereas Chloroflexi and Verrumicrobia abundance rose and reduced, respectively, after application of 5.0 percent by weight (T2-3) (Figure.5.23 A, B). In WBC-soil, but not CBC-soil, biochar treatment had a significant impact on proteobacteria groups. Regardless of the dosage, Alphaproteobacteria and Betaproteobacteria grew and reduced ($P = 0.001$ and $0.020$, respectively) following biochar application. In WBC-T-2-3 but not CBC-T-2-3 soils, biochar treatment had a significant impact on alphaproteobacteria groups. Regardless of the dosage, Actinobacteria and Betaproteobacteria grew and reduced ($P = 0.001$ and $0.020$, respectively) following biochar application.

## Summary

This study evaluated the potential advantages of two biochars, CBC and WBC, pyrolysed at 400 °C and 2h through the experiment of adsorption and desorption of $NH_4^+$-N and $NO_3^-$-N at a lab scale (Liu, X. et al., 2006). Results showed that both feedstocks, coffee ground and woodchip, produced similar biochar yields C with high and similar O/C, H/C ratios. The similar decreasing band intensity of hydroxyl (-OH), and aromatic (C=C) and (–COOH) functional groups for both CBC and WBC were due to carbon condensation. CEC of both biochars were also similar and were in a moderate range. However, ash content and C/N ratio of WBC was greater than CBC and also WHC. This means that WBC fixed higher C and would be considered as a better indicator for determining nutrient adsorption and desorption as compared to CBC.

The type of feedstock used and the temperature had a significant influence on the biochar's performance of physiochemical characteristics, which changed the biocahrs' N adsorption and desorption capacities. In this study, a variety of different models and kinetics were employed. With larger $r^2$ values, the Langmuir isotherm model fit the adsorption of $NH_4^+$-N to both biocahrs better than the Freundlich isotherm model. WBC released more nitrogen from the surface than CBC. The adsorption of $NH_4^+$-N and $NO_3^-$-N is best described by pseudo-first-order and pseudo-second-order kinetic models, respectively. As a result, we came to the conclusion that both biochars products may be utilized in situations where $NH_4^+$-N adsorption is a problem, whereas CBC can be used in situations where $NO_3^-$-N desorption is an issue. However, more study on the use of biochars to reduce $NO_3^-$-N pollution is required.

Regarding the application of biochar (CBC-400, WBC-400) in the plot experiment, different doses of biochar at 2.5%, and 5.0% (w/w) have not changed the microbial community in the last three and four years, which is confirmed. Therefore, we can add any fertilizer along with biochar application in future research.

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# CHATPER 6

# Conclusion

This study evaluated the potential of two biochars, CBC and WBC, pyrolysed at 400 °C and 2h on adsorption and desorption of $NH_4^+$-N and $NO_3^-$ -N at a lab scale. Results showed that both feedstocks, coffee ground and woodchip, produced similar biochar yields C with high and similar O/C, H/C ratios.

The similar decreasing band intensity of hydroxyl (-OH), and aromatic (C=C) and (–COOH) functional groups for both CBC and WBC were due to carbon condensation. CEC of both biochars were also similar and were in a moderate range. However, ash content and C/N ratio of WBC was greater than CBC. This means that WBC fixed higher C and would be considered as a better indicator for determining nutrient adsorption as compared to CBC.

The physiochemical properties of biochar were significantly influenced by the feedstock type and pyrolysis temperature, which in turn influenced the biochars' ability to adsorb and desorb nitrogen. In this study, several different models and kinetics were appliedThe results indicated that the Langmuir isotherm model suited the adsorption of $NH_4^+$-N to both biocahrs better than the Freundlich isotherm model, with higher $r^2$ values. In comparison to CBC400, WBC400 emitted more nitrogen from the surface. Pseudo-first-order and pseudo-second-order kinetic models, respectively, better suit the adsorption of $NH_4^+$-N and $NO_3^-$-N. As a result, we came to the conclusion that both biochars products may be utilized in situations where $NH_4^+$-N adsorption is a problem, whereas CBC can be used in situations where $NO_3^-$

-N desorption is an issue. However, more study on the use of biochars to reduce $NO_3^-$ -N pollution is required.

This potential of two aged biochars such as CBC and WBC, pyrolyzed at 400°C and 2h on batch adsorption and desorption of $NH_4^+$-N and $NO_3^-$-N at field condition. Results showed that both feedstocks, coffee ground and woodchip, produced similar biochar yields C with high and similar O/C, H/C ratios. CEC of both biochars were also similar and were in a moderate range. However, ash content and C/N ratio of WBC was greater than CBC. This means that WBC fixed higher C and would be considered as a better indicator for determining nutrient adsorption as compared to CBC.

The quantity of exchangeable cations and nutritional elements (e.g., $Ca^{2+}$, $K^+$, $Mg^{2+}$, and $Na^+$) might be raised following charcoal application in order to improve cation exchange capacity (CEC) and nutrient availability (Figure.4.9). As a consequence, $Ca^{2+}$ and $K^+$ were raised by 912 to 9.2 mg $g^{-1}$ for every year of soils-mixed CBC compared to control, whereas Mg and Na were marginally elevated by 2.13 to 2.42 mg/g and 1.6 to 1.66 mg $g^{-1}$ correspondingly in (Figure. 4.9a) and (Figure. 4.9b). $Mg^{2+}$ and $Na^+$, on the other hand, were not raised from 2.18 to 2.77 gm $g^{-1}$ and 0.30 to 1.120 mg $g^{-1}$. Ca and K levels in soil integrated with CBC were raised from 8.74 to 9.89 mg $g^{-1}$ and 7.55 to 8.83 mg $g^{-1}$, respectively, for the third year.

When biochar is used as a soil supplement over time, large levels of nutrient retention may be expected; hence, soils can be improved. However, large-scale research and long-term usage of biochar as a soil amendment are critical for predicting nutrient dynamics in soils treated with such materials. Application of biochar on a mass scale in extensive agriculture is expected to occur in the near future.

To achieve this final goal, there is an urgent need for long-term exposure or ageing assessments of the seasonal availability of main feedstocks for biochar production where biochar is intended to be used. Additionally, research studies should more frequently incorporate comprehensive economic analysis in addition to the more commonly studied implications of biochar in soil fertility and plant growth. Finally, while the logistic aspects of biochar distribution and further application in farmers' fields still remain a main hurdle at present, we expect these shortcomings will be increasingly and effectively addressed in the mid- to long-term.

Regarding the application of biochar (CBC-400, WBC-400) in the plot experiment, different doses of biochar at 2.5%, and 5.0% (w/w) have not changed the microbial community in the last three and four years, which is confirmed. Therefore, we can add any fertilizer along with biochar application in future research.

**Student Number:** 2017-33468

# Appendix A

## Figure 3.2 Exchangeable Cations of CBC, WBC, and Soil

**Table 1.** Data of Extractable Cation of $Ca^{2+}$, $K^{+}$, $Mg^{2+}$, and $Na^{+}$ (mg $g^{-1}$)

| No. | Sample | $Ca^{2+}$ | $K^{+}$ | $Mg^{2+}$ | $Na^{+}$ |
|---|---|---|---|---|---|
| 1 | CBC-400 | 1.738 | 21.115 | 1.039 | -0.002 |
| 2 | | 1.356 | 39.003 | 0.841 | -0.241 |
| 3 | | 1.259 | 41.51 | 0.782 | -0.234 |
| 4 | | 1.68 | 36.871 | 0.979 | 0.027 |
| 5 | | 1.312 | 40.976 | 0.795 | -0.165 |
| 6 | | 1.222 | 49.864 | 0.736 | -0.152 |
| 7 | | 1.64 | 19.15 | 1.031 | -1.149 |
| 8 | | 1.263 | 35.749 | 0.829 | -1.094 |
| 9 | | 1.213 | 37.857 | 0.768 | -1.01 |
| 10 | WBC-400 | 9.438 | 4.873 | 1.028 | 6.887 |
| 11 | | 9.874 | 4.98 | 1.017 | 6.999 |
| 12 | | 9.947 | 5.237 | 1.124 | 7.51 |
| 13 | | 9.269 | 33.008 | 0.975 | 6.98 |
| 14 | | 9.716 | 33.807 | 0.97 | 7.111 |
| 15 | | 9.807 | 33.342 | 1.062 | 7.61 |
| 16 | | 7.487 | 4.243 | 1.016 | 9.132 |
| 17 | | 7.699 | 4.438 | 1.012 | 7.867 |
| 18 | | 8.429 | 4.624 | 1.117 | 9.573 |
| 19 | Initial Soil | 13.906 | 0.944 | 3.532 | -0.088 |
| 20 | | 13.825 | 0.795 | 3.415 | -0.2 |
| 21 | | 13.528 | 0.771 | 3.265 | -0.257 |
| 22 | | 13.915 | 94.71 | 3.525 | -0.201 |
| 23 | | 13.839 | 75.041 | 3.356 | -0.274 |
| 24 | | 13.559 | 11.4745 | 3.19 | -0.268 |
| 25 | | 11.889 | 0.753 | 3.495 | -1.655 |
| 26 | | 11.657 | 0.638 | 3.373 | -0.09 |
| 27 | | 11.199 | 0.395 | 3.207 | -0.32 |

## Figure 3.7a. $NH_4^+$-N, adsorption kinetics on CBC, WBC, and soil

**Table 2.** Data of $NH_4^+$-N, adsorption kinetics on CBC, WBC, and soil

| **Time (min)** | **5** | **15** | **30** | **60** | **75** | **90** | **105** | **120** | **135** |
|---|---|---|---|---|---|---|---|---|---|
| 0.5 g CBC | 0.49 | 0.49 | 0.49 | 0.49 | 0.49 | 0.49 | 0.49 | 0.49 | 0.49 |
| | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 |
| | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 |
| AVE | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 |
| STD | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| | | | | | | | | | |
| **Time (min)** | **5** | **15** | **30** | **60** | **75** | **90** | **105** | **120** | **135** |
| Initial Con. | 100.5 | 101 | 102.1 | 103.4 | 103.5 | 105.7 | 106.4 | 108.4 | 108.5 |
| | 100.5 | 101 | 102.1 | 103.4 | 103.5 | 105.7 | 106.4 | 108.4 | 108.5 |
| | 100.5 | 101 | 102.1 | 103.4 | 103.5 | 105.7 | 106.4 | 108.4 | 108.5 |
| AVE | 100.5 | 101 | 102.1 | 103.4 | 103.5 | 105.7 | 106.4 | 108.4 | 108.5 |
| | | | | | | | | | |
| **Time (min)** | **5** | **15** | **30** | **60** | **75** | **90** | **105** | **120** | **135** |
| Equilibrium | 7.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.20 | 0.60 | 0.80 |
| | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.30 | 0.10 | 1.10 |
| | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.20 | 0.10 | 0.00 | 0.00 |
| AVE | 2.33 | 0.00 | 0.00 | 0.00 | 0.00 | 0.07 | 0.63 | 0.23 | 0.20 |
| STD | 4.04 | 0.00 | 0.00 | 0.00 | 0.00 | 0.12 | 0.57 | 0.32 | 0.10 |
| | | | | | | | | | |
| **Time (min)** | **5** | **15** | **30** | **60** | **75** | **90** | **105** | **120** | **135** |
| Qe | 9.48 | 10.24 | 10.35 | 10.48 | 10.49 | 10.72 | 10.77 | 10.93 | 10.92 |
| | 10.01 | 10.06 | 10.17 | 10.30 | 10.31 | 10.53 | 10.57 | 10.79 | 10.70 |
| | 10.01 | 10.06 | 10.17 | 10.30 | 10.31 | 10.50 | 10.58 | 10.79 | 10.80 |
| AVE | 9.83 | 10.12 | 10.23 | 10.36 | 10.37 | 10.58 | 10.64 | 10.84 | 10.81 |
| STD | 0.31 | 0.10 | 0.10 | 0.11 | 0.11 | 0.11 | 0.11 | 0.08 | 0.11 |
| | | | | | | | | | |

| **Time (min)** | **5** | **15** | **30** | **60** | **75** | **90** | **105** | **120** | **135** |
|---|---|---|---|---|---|---|---|---|---|
| Qt | 9.23 | 9.20 | 9.30 | 9.42 | 9.43 | 9.63 | 9.70 | 9.88 | 9.89 |
| | 9.02 | 9.06 | 9.16 | 9.28 | 9.29 | 9.48 | 9.55 | 9.73 | 9.75 |
| | 9.01 | 9.06 | 9.15 | 9.27 | 9.28 | 9.48 | 9.54 | 9.72 | 9.73 |
| AVE | 9.09 | 9.11 | 9.21 | 9.32 | 9.33 | 9.53 | 9.60 | 9.78 | 9.79 |
| STD | 0.12 | 0.08 | 0.08 | 0.08 | 0.08 | 0.09 | 0.09 | 0.09 | 0.09 |
| | | | | | | | | | |
| **Time (min)** | **5** | **15** | **30** | **60** | **75** | **90** | **105** | **120** | **135** |
| 0.5 g WBC | 0.49 | 0.49 | 0.49 | 0.49 | 0.49 | 0.49 | 0.49 | 0.49 | 0.49 |
| | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 |
| | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 |
| AVE | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 |
| STD | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| | | | | | | | | | |
| **Time(time)** | **5** | **15** | **30** | **60** | **75** | **90** | **105** | **120** | **135** |
| Initial Con. | 100.4 | 100.5 | 101 | 101.5 | 101.7 | 102.3 | 102.1 | 102.4 | 102.5 |
| | 100.4 | 100.5 | 101 | 101.5 | 101.7 | 102.3 | 102.1 | 102.4 | 102.5 |
| | 100.4 | 100.5 | 101 | 101.5 | 101.7 | 102.3 | 102.1 | 102.4 | 102.5 |
| AVE | 100 | 101 | 101 | 102 | 102 | 102 | 102 | 102 | 103 |
| | | | | | | | | | |
| **Time(time)** | **5** | **15** | **30** | **60** | **75** | **90** | **105** | **120** | **135** |
| Equilibrium | 0.0 | 0.0 | 0.0 | 0.1 | 0.2 | 0.0 | 3.5 | 54.7 | 20.7 |
| | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 31.7 |
| | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 35.0 |
| AVE | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | 1.2 | 18.2 | 29.1 |
| STD | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | 2.0 | 31.6 | 7.5 |
| | | | | | | | | | |
| **Time (min)** | **5** | **15** | **30** | **60** | **75** | **90** | **105** | **120** | **135** |
| Qe | 10.2 | 10.2 | 10.2 | 10.3 | 10.3 | 10.4 | 10.0 | 4.8 | 8.3 |
| | 10.0 | 10.0 | 10.1 | 10.1 | 10.1 | 10.2 | 10.2 | 10.2 | 7.1 |
| | 10.0 | 10.0 | 10.1 | 10.1 | 10.1 | 10.2 | 10.2 | 10.2 | 6.7 |
| AVE | 10.1 | 10.1 | 10.1 | 10.2 | 10.2 | 10.3 | 10.1 | 8.4 | 7.4 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| STD | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 3.1 | 0.8 |

| **Time (min)** | **5** | **15** | **30** | **60** | **75** | **90** | **105** | **120** | **135** |
|---|---|---|---|---|---|---|---|---|---|
| Qt | 9.15 | 9.16 | 9.20 | 9.25 | 9.27 | 9.32 | 9.34 | 9.89 | 9.55 |
| | 9.01 | 9.02 | 9.06 | 9.11 | 9.12 | 9.18 | 9.16 | 9.19 | 9.51 |
| | 9.00 | 9.01 | 9.06 | 9.10 | 9.12 | 9.17 | 9.15 | 9.18 | 9.54 |
| AVE | 9.05 | 9.06 | 9.11 | 9.15 | 9.17 | 9.22 | 9.22 | 9.42 | 9.53 |
| STD | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.10 | 0.41 | 0.02 |

| **Time (min)** | **5** | **15** | **30** | **60** | **75** | **90** | **105** | **120** | **135** |
|---|---|---|---|---|---|---|---|---|---|
| 0.5 g Soil | 5 | 15 | 30 | 60 | 75 | 90 | 105 | 120 | 135 |
| | 0.51 | 0.51 | 0.51 | 0.51 | 0.51 | 0.51 | 0.51 | 0.51 | 0.51 |
| | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 |
| | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 |
| AVE | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 |

| **Time (min)** | **5** | **15** | **30** | **60** | **75** | **90** | **105** | **120** | **135** |
|---|---|---|---|---|---|---|---|---|---|
| Initial Con. | 100.0 | 100.1 | 102.1 | 105.7 | 106.4 | 103.5 | 108.4 | 103.4 | 108.5 |
| | 100.0 | 100.1 | 102.1 | 105.7 | 106.4 | 103.5 | 108.4 | 103.4 | 108.5 |
| | 100.0 | 100.1 | 102.1 | 105.7 | 106.4 | 103.5 | 108.4 | 103.4 | 108.5 |
| AVE | 100.0 | 100.1 | 102.1 | 105.7 | 106.4 | 103.5 | 108.4 | 103.4 | 108.5 |

| **Time (min)** | **5** | **15** | **30** | **60** | **75** | **90** | **105** | **120** | **135** |
|---|---|---|---|---|---|---|---|---|---|
| Equilibrium | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 1.00 | 0.10 | 0.2 |
| | 0.10 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 |
| | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0 |
| AVE | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.3 | 0.0 | 0.1 |
| STD | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.6 | 0.1 | 0.2 |

| **Time (min)** | **5** | **15** | **30** | **60** | **75** | **90** | **105** | **120** | **135** |
|---|---|---|---|---|---|---|---|---|---|
| Qe | 9.89 | 9.90 | 10.09 | 10.45 | 10.52 | 10.23 | 10.62 | 10.21 | 10.71 |
| | 9.98 | 10.0 | 10.20 | 10.56 | 10.63 | 10.34 | 10.83 | 10.33 | 10.84 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 10.05 | 10.06 | 10.26 | 10.62 | 10.69 | 10.40 | 10.89 | 10.39 | 10.90 |
| AVE | 9.97 | 9.99 | 10.19 | 10.55 | 10.62 | 10.33 | 10.78 | 10.31 | 10.82 |
| STD | 0.08 | 0.08 | 0.08 | 0.09 | 0.09 | 0.09 | 0.14 | 0.09 | 0.10 |
| | | | | | | | | | |
| **Time (min)** | **5** | **15** | **30** | **60** | **75** | **90** | **105** | **120** | **135** |
| Qt | 8.91 | 8.92 | 9.10 | 9.42 | 9.48 | 9.22 | 9.67 | 9.21 | 9.67 |
| | 8.99 | 9.00 | 9.18 | 9.51 | 9.57 | 9.31 | 9.75 | 9.30 | 9.76 |
| | 9.04 | 9.05 | 9.23 | 9.56 | 9.62 | 9.36 | 9.80 | 9.35 | 9.81 |
| AVE | 8.98 | 8.99 | 9.17 | 9.49 | 9.56 | 9.30 | 9.74 | 9.29 | 9.75 |
| STD | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 |

**Figure 3.7b. $NO_3^-$-N desorption onto CBC, WBC and Initial soil**

**Table 3.** Data of $NO_3^-$-N, adsorption kinetics on CBC, WBC, and soil

| **Time(min)** | **5** | **15** | **30** | **60** | **70** | **90** | **105** | **120** | **135** |
|---|---|---|---|---|---|---|---|---|---|
| 0.5 g WBC | 0.49 | 0.49 | 0.49 | 0.49 | 0.49 | 0.49 | 0.49 | 0.49 | 0.49 |
| | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 |
| | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 |
| AVE | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 |
| STD | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| | | | | | | | | | |
| **Time(min)** | **5** | **15** | **30** | **60** | **70** | **90** | **105** | **120** | **135** |
| Initial Con. | 82.7 | 83.1 | 83.4 | 84.6 | 84.7 | 85.3 | 85.9 | 89.3 | 104.5 |
| | 82.7 | 83.1 | 83.4 | 84.6 | 84.7 | 85.3 | 85.9 | 89.3 | 104.5 |
| | 82.7 | 83.1 | 83.4 | 84.6 | 84.7 | 85.3 | 85.9 | 89.3 | 104.5 |
| AVE | 82.7 | 83.1 | 83.4 | 84.6 | 84.7 | 85.3 | 85.9 | 89.3 | 104.5 |
| STD | 0 | 0 | 0 | 0 | 0 | 0 | 2E-1 | 0 | 0 |
| | | | | | | | | | |

| **Time(min)** | **5** | **15** | **30** | **60** | **70** | **90** | **105** | **120** | **135** |
|---|---|---|---|---|---|---|---|---|---|
| Equilibrium | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.80 | 0.20 | 0.30 |
| | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 3.00 | 0.10 | 0.00 |
| | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.20 | 1.50 | 1.00 | 0.00 |
| AVE | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.07 | 1.77 | 0.43 | 1.77 |
| STD | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.12 | 1.12 | 0.49 | 1.12 |

| **Time(min)** | **5** | **15** | **30** | **60** | **70** | **90** | **105** | **120** | **135** |
|---|---|---|---|---|---|---|---|---|---|
| Qe | 8.38 | 8.43 | 8.46 | 8.58 | 8.59 | 8.65 | 8.63 | 9.03 | 4.21 |
| | 8.24 | 8.28 | 8.31 | 8.43 | 8.44 | 8.50 | 8.26 | 8.89 | 4.05 |
| | 8.23 | 8.27 | 8.30 | 8.42 | 8.43 | 8.47 | 8.40 | 8.79 | 4.10 |
| AVE | 8.29 | 8.33 | 8.36 | 8.48 | 8.49 | 8.54 | 8.43 | 8.90 | 4.12 |
| STD | 0.08 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 | 0.18 | 0.12 | 0.08 |

| **Time(min)** | **5** | **15** | **30** | **60** | **70** | **90** | **105** | **120** | **135** |
|---|---|---|---|---|---|---|---|---|---|
| $Q_t$ | 7.53 | 7.57 | 7.60 | 7.71 | 7.72 | 7.77 | 7.83 | 8.14 | 10.17 |
| | 7.42 | 7.46 | 7.48 | 7.59 | 7.60 | 7.65 | 7.74 | 8.01 | 10.01 |
| | 7.41 | 7.45 | 7.48 | 7.59 | 7.59 | 7.65 | 7.72 | 8.02 | 10.00 |
| AVE | 7.46 | 7.49 | 7.52 | 7.63 | 7.64 | 7.69 | 7.76 | 8.06 | 10.06 |
| STD | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.06 | 0.07 | 0.10 |

| **Time(min)** | **5** | **15** | **30** | **60** | **75** | **90** | **105** | **120** | **135** |
|---|---|---|---|---|---|---|---|---|---|
| 0.5 g Init- Soil | 0.51 | 0.51 | 0.51 | 0.51 | 0.51 | 0.51 | 0.51 | 0.51 | 0.51 |
| | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 |
| | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 |
| AVE | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 |

| **Time(min)** | **5** | **15** | **30** | **60** | **75** | **90** | **105** | **120** | **135** |
|---|---|---|---|---|---|---|---|---|---|
| Initial Con. | 67.15 | 75.05 | 80 | 80.7 | 81.8 | 82.4 | 86.05 | 100.6 | 105.5 |
| | 67.15 | 75.05 | 80 | 80.7 | 81.8 | 82.4 | 86.05 | 100.6 | 105.5 |
| | 67.15 | 75.05 | 80 | 80.7 | 81.8 | 82.4 | 86.05 | 100.6 | 105.5 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| AVE | 67.15 | 75.05 | 80 | 80.7 | 81.8 | 82.4 | 86.05 | 100.6 | 105.5 |

| **Time(min)** | **5** | **15** | **30** | **60** | **75** | **90** | **105** | **120** | **135** |
|---|---|---|---|---|---|---|---|---|---|
| Equilibrium | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 1.00 | 0.50 | 0.2 |
| | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0 |
| | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0 |
| AVE | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.3 | 0.2 | 0.1 |
| STD | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.6 | 0.3 | 0.2 |

| **Time(min)** | **5** | **15** | **30** | **60** | **75** | **90** | **105** | **120** | **135** |
|---|---|---|---|---|---|---|---|---|---|
| Qe | 6.64 | 7.42 | 7.91 | 7.98 | 8.09 | 8.15 | 8.41 | 9.90 | 10.41 |
| | 6.71 | 7.50 | 7.99 | 8.06 | 8.17 | 8.23 | 8.60 | 10.05 | 10.54 |
| | 6.75 | 7.54 | 8.04 | 8.11 | 8.22 | 8.28 | 8.65 | 10.11 | 10.60 |
| AVE | 6.70 | 7.49 | 7.98 | 8.05 | 8.16 | 8.22 | 8.55 | 10.02 | 10.52 |
| STD | 0.06 | 0.06 | 0.07 | 0.07 | 0.07 | 0.07 | 0.13 | 0.11 | 0.10 |

| **Time(min)** | **5** | **15** | **30** | **60** | **75** | **90** | **105** | **120** | **135** |
|---|---|---|---|---|---|---|---|---|---|
| $Q_t$ | 5.98 | 6.69 | 7.13 | 7.19 | 7.29 | 7.34 | 7.68 | 8.97 | 9.40 |
| | 6.04 | 6.75 | 7.20 | 7.26 | 7.36 | 7.41 | 7.74 | 9.05 | 9.49 |
| | 6.07 | 6.78 | 7.23 | 7.30 | 7.39 | 7.45 | 7.78 | 9.09 | 9.54 |
| AVE | 6.03 | 6.74 | 7.18 | 7.25 | 7.35 | 7.40 | 7.73 | 9.04 | 9.48 |
| STD | 0.04 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.06 | 0.07 |

**Figure 3.3. 4 Electrical conductivity of soil salinity (dS $m^{-1}$)**

**Table 4.** Data of Electrical conductivity of soil salinity (dS $m^{-1}$)

| **Initial Soil** | **CBC** | **WBC** | **Year-1** | | | | **Year-2** | | | | **Year-3** | | | | **Year-4** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | **CBC-Soil** | | **WBC-Soil** | | **CBC-Soil** | | **WBC-Soil** | | **CBC-Soil** | | **WBC Soil** | | **CBC Soil** | | **WBC Soil** | |
| | | | **2.5%** | **5%** | **2.5%** | **5%** | **2.5%** | **5%** | **2.5%** | **5%** | **2.5%** | **5%** | **2.5%** | **5%** | **2.5%** | **5%** | **2.5%** | **5%** |
| 3.83 | 5.02 | 4.92 | 3.54 | 3.84 | 3.64 | 3.94 | 3.54 | 3.94 | 3.65 | 3.98 | 3.62 | 3.7 | 3.64 | 3.8 | 3.9 | 3.94 | 3.86 | 3.6 |
| 4.17 | 5.01 | 4.9 | 3.49 | 3.85 | 3.49 | 3.85 | 3.69 | 4.01 | 3.75 | 3.98 | 3.73 | 3.86 | 3.86 | 3.85 | 3.83 | 3.91 | 3.82 | 3.78 |
| 3.81 | 5.07 | 4.9 | 3.71 | 3.64 | 3.71 | 3.64 | 3.51 | 3.64 | 3.84 | 3.63 | 3.7 | 3.79 | 3.65 | 3.95 | 3.87 | 3.89 | 3.69 | 3.77 |
| 3.94 | 5.03 | 4.91 | 3.58 | 3.78 | 3.61 | 3.81 | 3.58 | 3.86 | 3.75 | 3.86 | 3.68 | 3.78 | 3.72 | 3.87 | 3.87 | 3.91 | 3.79 | 3.72 |
| 0.20 | 0.03 | 0.01 | 0.12 | 0.12 | 0.11 | 0.15 | 0.10 | 0.20 | 0.10 | 0.20 | 0.06 | 0.08 | 0.12 | 0.08 | 0.04 | 0.03 | 0.09 | 0.10 |

# Appendix B

## Figure 4. 9 Extractable Cation of $Ca^{2+}$, $K^+$, $Mg^{2+}$ and $Na^+$ of CBC, WBC, and Soil from first, second and third year

**Table 1.** Data of the first seasonal crop of soil –CBC mixture (mg $g^{-1}$)

| No. | Samples | $Ca^{2+}$ | $K^+$ | $Mg^{2+}$ | $Na^+$ |
|---|---|---|---|---|---|
| 1 | Initial Soil | 13.906 | 0.944 | 3.532 | 0.088 |
| 2 | | 13.825 | 0.795 | 3.415 | 0.200 |
| 3 | | 13.528 | 0.771 | 3.265 | 0.257 |
| 4 | | 13.915 | 9.471 | 3.525 | 0.201 |
| 5 | | 13.839 | 7.504 | 3.356 | 0.274 |
| 6 | | 13.559 | 11.475 | 3.190 | 0.268 |
| 7 | | 11.889 | 0.753 | 3.495 | 1.655 |
| 8 | | 11.657 | 0.638 | 3.373 | 0.090 |
| 9 | | 11.199 | 0.395 | 3.207 | 0.320 |
| 10 | 2018-Soil-CBC-T-1-1 | 8.870 | 4.047 | 2.204 | 0.202 |
| 11 | | 9.090 | 4.349 | 2.169 | 0.219 |
| 12 | | 8.301 | 4.005 | 2.099 | 0.219 |
| 13 | | 8.774 | 14.367 | 2.135 | 0.191 |
| 14 | | 8.980 | 14.650 | 2.108 | 0.205 |
| 15 | | 8.173 | 17.898 | 2.038 | 0.210 |
| 16 | | 7.432 | 3.734 | 2.175 | 0.917 |
| 17 | | 7.312 | 3.975 | 2.149 | 0.161 |
| 18 | | 7.075 | 3.841 | 2.067 | 0.090 |
| 19 | 2018-Soil-CBC-T-2-1 | 9.342 | 2.255 | 2.379 | -0.194 |
| 20 | | 9.843 | 2.407 | 2.521 | -0.168 |
| 21 | | 9.802 | 2.184 | 2.454 | -0.234 |
| 22 | | 9.234 | 16.579 | 2.294 | -0.236 |
| 23 | | 9.713 | 20.865 | 2.426 | -0.247 |
| 24 | | 9.670 | 19.405 | 2.369 | -0.197 |
| 25 | | 7.906 | 1.935 | 2.375 | -0.437 |
| 26 | | 8.394 | 2.035 | 2.504 | -1.603 |

| | | | | | |
|---|---|---|---|---|---|
| 27 | | 8.289 | 1.988 | 2.426 | 0.186 |
| 28 | 2019-Soil-CBC-T-1-1 | 11.313 | 2.275 | 2.903 | -0.204 |
| 29 | | 10.471 | 2.025 | 2.679 | -0.207 |
| 30 | | 11.299 | 2.392 | 2.883 | -0.119 |
| 31 | | 11.137 | 19.886 | 2.786 | -0.143 |
| 32 | | 10.348 | 28.479 | 2.579 | -0.190 |
| 33 | | 11.154 | 27.108 | 2.767 | -0.119 |
| 34 | | 9.421 | 1.899 | 2.878 | 0.132 |
| 35 | | 8.745 | 1.639 | 2.655 | -1.006 |
| 36 | | 9.389 | 2.118 | 2.864 | -0.589 |
| 37 | 2019-Soil-CBC-T-2-1 | 10.881 | 0.683 | 2.273 | 0.151 |
| 38 | | 10.748 | 0.732 | 2.222 | 0.184 |
| 39 | | 10.035 | 0.881 | 2.161 | 0.138 |
| 40 | | 10.690 | 27.615 | 2.162 | 0.214 |
| 41 | | 10.395 | 30.093 | 2.106 | 0.217 |
| 42 | | 10.889 | 30.335 | 2.059 | 0.165 |
| 43 | | 9.010 | 0.676 | 2.257 | 1.120 |
| 44 | | 8.715 | 0.526 | 2.209 | -0.487 |
| 45 | | 8.496 | 0.363 | 2.166 | -0.102 |
| 46 | 2020-Soil-CBC-T-1-1 | 11.313 | 0.683 | 2.923 | 0.551 |
| 47 | | 10.471 | 0.732 | 2.779 | 0.284 |
| 48 | | 11.399 | 0.851 | 2.853 | 0.138 |
| 49 | | 11.137 | 27.615 | 2.796 | 0.214 |
| 50 | | 10.348 | 30.093 | 2.579 | 0.218 |
| 51 | | 11.154 | 30.335 | 2.767 | 0.265 |
| 52 | | 9.721 | 0.676 | 2.878 | -1.120 |
| 53 | | 8.775 | 0.526 | 2.635 | -0.447 |
| 54 | | 9.389 | 0.343 | 2.864 | -0.102 |
| 55 | 2020-Soil-CBC-T-2-1 | 10.851 | 0.683 | 2.373 | 0.151 |
| 56 | | 10.548 | 0.772 | 2.222 | 0.184 |
| 57 | | 11.033 | 0.981 | 2.262 | 0.138 |
| 58 | | 10.788 | 27.515 | 2.362 | 0.284 |
| 59 | | 10.395 | 30.493 | 2.106 | 0.517 |

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| 60 |  | 10.786 | 30.835 | 2.359 | 0.265 |
| 61 |  | 9.010 | 0.651 | 2.257 | 1.120 |
| 62 |  | 8.715 | 0.557 | 2.209 | 0.447 |
| 63 |  | 8.496 | 0.369 | 2.166 | 0.102 |

**Table 2.** Data of the four-year seasonal crops of soil WBC mixture

| No. | Samples | $Ca^{2+}$ | $K^{+}$ | $Mg^{2+}$ | $Na^{+}$ |
|---|---|---|---|---|---|
| 1 | Initial soil | 13.906 | 0.944 | 3.532 | 0.088 |
| 2 |  | 13.825 | 0.795 | 3.415 | 0.200 |
| 3 |  | 13.528 | 0.771 | 3.265 | 0.257 |
| 4 |  | 13.915 | 9.471 | 3.525 | 0.201 |
| 5 |  | 13.839 | 7.504 | 3.356 | 0.274 |
| 6 |  | 13.559 | 11.475 | 3.190 | 0.268 |
| 7 |  | 11.889 | 0.7530 | 3.495 | 1.655 |
| 8 |  | 11.657 | 0.6383 | 3.373 | 0.090 |
| 9 |  | 11.199 | 0.3950 | 3.207 | 0.320 |
| 10 | 2018-SOIL-WBC-T1-1 | 10.768 | 3.072 | 1.932 | -0.046 |
| 11 |  | 7.377 | 2.103 | 1.833 | -0.070 |
| 12 |  | 19.020 | 2.599 | 3.551 | 0.103 |
| 13 |  | 7.715 | 5.615 | 1.786 | 0.080 |
| 14 |  | 7.367 | 5.409 | 1.710 | 0.002 |
| 15 |  | 19.120 | 5.271 | 3.291 | 0.220 |
| 16 |  | 7.996 | 2.538 | 1.923 | -0.523 |
| 17 |  | 7.610 | 1.766 | 1.844 | 0.102 |
| 18 |  | 14.061 | 2.171 | 3.567 | 0.568 |
| 19 | 2018-Soil-WBC-T-2-1 | 8.408 | 1.728 | 2.195 | 0.245 |
| 20 |  | 7.741 | 1.575 | 2.009 | 0.240 |
| 21 |  | 7.959 | 1.531 | 1.999 | 0.274 |
| 22 |  | 8.361 | 4.620 | 2.019 | 0.379 |
| 23 |  | 7.704 | 5.225 | 1.844 | 0.355 |
| 24 |  | 5.965 | 5.186 | 1.830 | 0.331 |
| 25 |  | 8.753 | 1.288 | 2.206 | 2.159 |
| 26 |  | 7.951 | 1.177 | 2.021 | -1.726 |

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| 27 |  | 8.249 | 1.304 | 2.011 | -1.712 |
| 28 | 2019-Soil-WBC-T-1-1 | 6.148 | 1.338 | 1.633 | -0.033 |
| 29 |  | 6.611 | 1.335 | 1.293 | -0.033 |
| 30 |  | 6.074 | 1.125 | 1.236 | -0.052 |
| 31 |  | 6.112 | 6.063 | 1.495 | 0.057 |
| 32 |  | 6.585 | 6.261 | 1.170 | 0.131 |
| 33 |  | 6.031 | 5.649 | 1.121 | 0.044 |
| 34 |  | 6.795 | 1.125 | 1.634 | 2.280 |
| 35 |  | 5.337 | 1.124 | 1.292 | 0.334 |
| 36 |  | 5.223 | 0.849 | 1.245 | -3.002 |
| 37 | 2019-Soil-WBC-T-2-1 | 5.084 | 5.019 | 1.197 | -0.215 |
| 38 |  | 5.081 | 5.608 | 1.314 | -0.150 |
| 39 |  | 4.935 | 4.721 | 1.228 | -0.170 |
| 40 |  | 5.039 | 6.002 | 1.089 | -0.100 |
| 41 |  | 5.044 | 5.639 | 1.195 | -0.068 |
| 42 |  | 4.912 | 5.969 | 1.111 | -0.148 |
| 43 |  | 4.500 | 4.152 | 1.202 | -0.820 |
| 44 |  | 4.721 | 5.073 | 1.335 | -1.600 |
| 45 |  | 4.439 | 3.952 | 1.243 | -1.902 |
| 46 | 2020-Soil-WBC-T-1-1 | 5.084 | 5.019 | 1.197 | -0.215 |
| 47 |  | 5.081 | 5.608 | 1.314 | -0.150 |
| 48 |  | 4.935 | 4.721 | 1.228 | -0.170 |
| 49 |  | 5.039 | 6.002 | 1.089 | -0.100 |
| 50 |  | 5.044 | 5.639 | 1.195 | -0.068 |
| 51 |  | 4.912 | 5.964 | 1.111 | -0.148 |
| 52 |  | 4.500 | 4.152 | 1.202 | -0.820 |
| 53 |  | 4.721 | 5.073 | 1.335 | -1.600 |
| 54 |  | 4.439 | 3.952 | 1.243 | -1.902 |
| 55 | 2020-Soil-WBC-T-2-1 | 5.084 | 5.019 | 1.197 | -0.215 |
| 56 |  | 5.081 | 5.608 | 1.314 | -0.150 |
| 57 |  | 4.935 | 4.721 | 1.228 | -0.170 |
| 58 |  | 5.039 | 6.002 | 1.089 | -0.100 |
| 59 |  | 5.044 | 5.639 | 1.195 | -0.068 |

| | | | | | |
|---|---|---|---|---|---|
| 60 | | 4.934 | 5.964 | 1.111 | -0.148 |
| 61 | | 4.500 | 4.152 | 1.202 | -0.820 |
| 62 | | 4.721 | 5.073 | 1.335 | -1.600 |
| 63 | | 4.528 | 3.952 | 1.243 | -1.902 |

**Figure 4.3.4.10a Effects of CBC, and WBC on total dry weight Pak Choi Yields**

**Table 3. 12.** Effects of CBC and WBC on Pak Choi Yields through 4 seasonal crop.

**CBC Application on Total Dry Weight of Pak Choi Productivity (g / m2)**

| No. | Year-1 | | Year-2 | | Year-3 | | Year-4 | |
|---|---|---|---|---|---|---|---|---|
| | T-1 | T-2 | T-1 | T-2 | T-1 | T-2 | T-1 | T-2 |
| 1 | 1.575 | 0.765 | 9.998 | 6.225 | 21.480 | 24.440 | 11.940 | 7.650 |
| 2 | 0.785 | 0.310 | 6.020 | 6.815 | 16.100 | 24.730 | 10.330 | 11.220 |
| 3 | 2.288 | 0.708 | 3.673 | 8.025 | 16.550 | 26.100 | 20.360 | 26.310 |
| AVE | 1.549 | 0.594 | 6.563 | 7.022 | 18.043 | 25.090 | 14.210 | 15.060 |
| STD | 0.752 | 0.248 | 3.197 | 0.918 | 2.985 | 0.887 | 5.387 | 9.905 |

**WBC Application on Total Dry Weight of Pak Choi Productivity (g / m2)**

| No. | Year-1 | | Year-2 | | Year-3 | | Year-4 | |
|---|---|---|---|---|---|---|---|---|
| | T-1 | T-2 | T-1 | T-2 | T-1 | T-2 | T-1 | T-2 |
| 1 | 1.998 | 3.330 | 7.733 | 8.020 | 30.520 | 35.640 | 20.340 | 26.230 |
| 2 | 1.868 | 1.390 | 11.175 | 25.713 | 27.710 | 37.640 | 27.460 | 15.040 |
| 3 | 0.420 | 1.428 | 9.743 | 15.373 | 24.360 | 41.590 | 14.740 | 23.740 |
| AVE | 1.428 | 2.049 | 9.550 | 16.368 | 27.530 | 38.290 | 20.847 | 21.670 |
| STD | 0.876 | 1.109 | 1.729 | 8.888 | 3.084 | 3.028 | 6.375 | 5.875 |

**Figure 4.3.4.10b Effects of CBC, and WBC on total wet weight Pak Choi Yields**

**Table 4.** Effects of CBC, and WBC on total wet weight Pak Choi Yields

**CBC Application on Total wet Weight of Pak Choi Productivity (g / m$^2$)**

| No. | Year-1 | | Year-2 | | Year-3 | | Year-4 | |
|---|---|---|---|---|---|---|---|---|
| | T-1 | T-2 | T-1 | T-2 | T-1 | T-2 | T-1 | T-2 |
| 1 | 1.270 | 5.300 | 110.760 | 94.195 | 212.460 | 206.140 | 150.420 | 152.740 |
| 2 | 3.097 | 1.888 | 77.125 | 103.460 | 135.920 | 199.810 | 162.310 | 102.210 |
| 3 | 0.540 | 8.683 | 101.675 | 94.430 | 127.520 | 136.890 | 164.000 | 230.000 |
| AVE | 1.636 | 5.290 | 96.520 | 97.362 | 158.633 | 180.947 | 158.910 | 161.650 |
| STD | 1.317 | 3.398 | 17.400 | 5.283 | 46.804 | 38.285 | 7.401 | 64.359 |

**WBC Application on Total wet Weight of Pak Choi Productivity (g / m$^2$)**

| No. | Year-1 | | Year-2 | | Year-3 | | Year-4 | |
|---|---|---|---|---|---|---|---|---|
| | T-1 | T-2 | T-1 | T-2 | T-1 | T-2 | T-1 | T-2 |
| 1 | 8.063 | 10.020 | 91.445 | 121.847 | 231.730 | 247.340 | 144.120 | 200.600 |
| 2 | 11.178 | 10.123 | 123.185 | 142.117 | 129.080 | 153.230 | 231.520 | 247.800 |
| 3 | 1.478 | 1.673 | 124.560 | 124.167 | 110.670 | 167.080 | 151.540 | 152.370 |
| AVE | 6.906 | 7.272 | 113.063 | 129.377 | 157.160 | 189.217 | 175.727 | 200.257 |
| STD | 4.952 | 4.849 | 18.735 | 11.094 | 65.232 | 50.810 | 48.461 | 47.716 |

**Figure 4.19. Effects of CBC and WBC on Water Holding Capacity (WHC)**

**Table 5.** Biochar application on water holding capacity of soils (%)

**CBC Application on Water Holding Capacity of Soils (WHC) (%)**

| No. | Year-1 | | Year-2 | | Year-3 | | Year-4 | |
|---|---|---|---|---|---|---|---|---|
| | T-1 | T-2 | T-1 | T-2 | T-1 | T-2 | T-1 | T-2 |
| 1 | 40.609 | 48.018 | 41.609 | 58.018 | 54.065 | 62.627 | 66.175 | 65.390 |
| 2 | 42.708 | 49.345 | 52.708 | 61.345 | 64.462 | 63.307 | 66.126 | 64.957 |
| 3 | 44.165 | 50.011 | 59.165 | 50.011 | 68.356 | 64.475 | 65.657 | 64.966 |
| AVE | 42.494 | 49.125 | 51.161 | 56.458 | 62.294 | 63.470 | 65.986 | 65.104 |
| STD | 1.787 | 0.829 | 8.880 | 5.826 | 0.237 | 0.093 | 0.029 | 0.023 |

**WBC on Water holding capacity of soils (%)**

| No. | Year-1 | | Year-2 | | Year-3 | | Year-4 | |
|---|---|---|---|---|---|---|---|---|
| | T-1 | T-2 | T-1 | T-2 | T-1 | T-2 | T-1 | T-2 |
| 1 | 47.692 | 56.205 | 57.692 | 66.205 | 63.658 | 63.410 | 63.503 | 67.900 |
| 2 | 47.290 | 55.521 | 47.290 | 65.521 | 63.510 | 62.901 | 63.632 | 73.312 |
| 3 | 48.464 | 67.783 | 58.464 | 67.783 | 66.288 | 62.422 | 63.802 | 63.435 |
| AVE | 47.815 | 59.836 | 54.482 | 66.503 | 64.485 | 62.911 | 63.646 | 68.216 |
| STD | 0.060 | 0.116 | 0.060 | 0.116 | 0.156 | 0.049 | 0.015 | 0.026 |

# Appendix C

### Figure 5. 20 Total Soil Organic Matter and Total Nitrogen of initial soil, Soil- CBC mixture, and Soil- WBC mixture

**Table 1.** Total Organic Matter of Soil –CBC mixture (g C kg$^{-1}$)

| No. | Sample Names | A490 | A375 | A375/A490 | ug C | Soil (g) | mg C / g Soil |
|---|---|---|---|---|---|---|---|
| 1 | 10 Initial-1 | 0.288 | 0.921 | 3.198 | 14.705 | 0.1003 | 0.147 |
| 2 | 11 Initial-2 | 0.283 | 0.927 | 3.276 | 14.977 | 0.1001 | 0.150 |
| 3 | 12 Initial-3 | 0.280 | 0.926 | 3.307 | 15.087 | 0.1010 | 0.149 |
| 4 | 13 C-Y1-T0-1 | 0.292 | 0.958 | 3.281 | 14.995 | 0.1075 | 0.139 |
| 5 | 14 C-Y1-T0-2 | 0.295 | 0.946 | 3.207 | 14.736 | 0.1062 | 0.139 |
| 6 | 15 C-Y1-T0-3 | 0.299 | 0.947 | 3.167 | 14.598 | 0.1058 | 0.138 |
| 7 | 16 C-Y1-T1-1 | 0.295 | 0.949 | 3.217 | 14.772 | 0.1013 | 0.146 |
| 8 | 17 C-Y1-T1-2 | 0.299 | 0.942 | 3.151 | 14.539 | 0.1016 | 0.143 |
| 9 | 18 C-Y1-T1-3 | 0.289 | 0.959 | 3.318 | 15.126 | 0.1011 | 0.150 |
| 10 | 19 C-Y1-T2-1 | 0.286 | 0.956 | 3.343 | 15.211 | 0.1042 | 0.146 |
| 11 | 20 C-Y1-T2-2 | 0.281 | 0.952 | 3.388 | 15.369 | 0.1032 | 0.149 |
| 12 | 21 C-Y1-T2-3 | 0.276 | 0.946 | 3.428 | 15.508 | 0.1028 | 0.151 |
| 13 | 22 C-Y2-T0-1 | 0.295 | 0.956 | 3.241 | 14.855 | 0.1069 | 0.139 |
| 14 | 23 C-Y2-T0-2 | 0.295 | 0.956 | 3.241 | 14.855 | 0.1052 | 0.141 |
| 15 | 24 C-Y2-T0-3 | 0.289 | 0.951 | 3.291 | 15.029 | 0.1048 | 0.143 |
| 16 | 25 C-Y2-T1-1 | 0.263 | 0.958 | 3.643 | 16.260 | 0.1026 | 0.158 |
| 17 | 26 C-Y2-T1-2 | 0.260 | 0.952 | 3.662 | 16.326 | 0.1031 | 0.158 |
| 18 | 27 C-Y2-T1-3 | 0.258 | 0.962 | 3.729 | 16.561 | 0.1027 | 0.161 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 19 | 28 C-Y2-T2-1 | 0.244 | 0.969 | 3.971 | 17.409 | 0.1000 | 0.174 |
| 20 | 29 C-Y2-T2-2 | 0.247 | 0.967 | 3.915 | 17.212 | 0.1003 | 0.172 |
| 21 | 30 C-Y2-T2-3 | 0.245 | 0.972 | 3.967 | 17.395 | 0.1007 | 0.173 |
| 22 | 31 C-Y3-T0-1 | 0.274 | 0.958 | 3.496 | 15.748 | 0.1047 | 0.150 |
| 23 | 32 C-Y3-T0-2 | 0.271 | 0.955 | 3.524 | 15.845 | 0.1051 | 0.151 |
| 24 | 33 C-Y3-T0-3 | 0.270 | 0.952 | 3.526 | 15.852 | 0.1041 | 0.152 |
| 25 | 34 C-Y3-T1-1 | 0.255 | 0.996 | 3.906 | 17.180 | 0.1021 | 0.168 |
| 26 | 35 C-Y3-T1-2 | 0.249 | 0.999 | 4.012 | 17.552 | 0.1019 | 0.172 |
| 27 | 36 C-Y3-T1-3 | 0.251 | 0.991 | 3.948 | 17.328 | 0.1012 | 0.171 |
| 28 | 37 C-Y3-T2-1 | 0.232 | 1.003 | 4.323 | 18.640 | 0.1062 | 0.176 |
| 29 | 38 C-Y3-T2-2 | 0.235 | 1.008 | 4.289 | 18.521 | 0.1040 | 0.178 |
| 30 | 39 C-Y3-T2-3 | 0.233 | 1.007 | 4.322 | 18.635 | 0.105 | 0.177 |
| 31 | 40 C-Y4-T1 | 0.255 | 0.958 | 3.757 | 16.659 | 0.100 | 0.101 |
| 32 | 41 C-Y4-T1 | 0.259 | 0.950 | 3.668 | 16.348 | 0.100 | 0.100 |
| 33 | 42C-Y4-T1 | 0.258 | 0.975 | 3.779 | 16.737 | 0.101 | 0.101 |
| 34 | 43C-Y4-T2 | 0.224 | 0.979 | 4.371 | 18.805 | 0.101 | 0.100 |
| 35 | 44 C-Y4-T2 | 0.256 | 0.972 | 3.797 | 16.799 | 0.101 | 0.100 |
| 36 | 45 C-Y4-T2 | 0.242 | 0.997 | 4.120 | 17.928 | 0.101 | 0.100 |

**Table 2.** Total Organic Matter of Soil –WBC mixture (g C kg$^{-1}$)

| No. | Sample Names | A490 | A375 | A375/A490 | ug C | Soil (g) | mg C / g Soil |
|---|---|---|---|---|---|---|---|
| 1 | 10 Initial-1 | 0.288 | 0.921 | 3.198 | 14.705 | 0.100 | 0.147 |
| 2 | 11 Initial-2 | 0.283 | 0.927 | 3.276 | 14.977 | 0.100 | 0.150 |
| 3 | 12 Initial-3 | 0.280 | 0.926 | 3.307 | 15.087 | 0.101 | 0.149 |
| 4 | 13 W-Y1-T0-1 | 0.246 | 0.980 | 3.984 | 17.453 | 0.106 | 0.164 |
| 5 | 14 W-Y1-T0-2 | 0.248 | 0.982 | 3.960 | 17.368 | 0.105 | 0.165 |
| 6 | 15 W-Y1-T0-3 | 0.246 | 0.984 | 4.000 | 17.509 | 0.105 | 0.167 |
| 7 | 16 W-Y1-T1-1 | 0.238 | 0.985 | 4.139 | 17.994 | 0.108 | 0.167 |
| 8 | 17 W-Y1-T1-2 | 0.240 | 0.986 | 4.108 | 17.888 | 0.105 | 0.170 |
| 9 | 18 W-Y1-T1-3 | 0.235 | 0.989 | 4.209 | 18.238 | 0.106 | 0.172 |
| 10 | 19 W-Y1-T2-1 | 0.218 | 1.002 | 4.596 | 19.594 | 0.102 | 0.193 |
| 11 | 20 W-Y1-T2-2 | 0.221 | 1.000 | 4.525 | 19.345 | 0.101 | 0.191 |
| 12 | 21 W-Y1-T2-3 | 0.215 | 1.006 | 4.679 | 19.884 | 0.101 | 0.197 |
| 13 | 22 W-Y2-T0-1 | 0.268 | 0.982 | 3.664 | 16.335 | 0.102 | 0.160 |
| 14 | 23 W-Y2-T0-2 | 0.265 | 0.984 | 3.713 | 16.507 | 0.101 | 0.164 |
| 15 | 24 W-Y2-T0-3 | 0.264 | 0.981 | 3.716 | 16.516 | 0.100 | 0.165 |
| 16 | 25 W-Y2-T1-1 | 0.244 | 0.990 | 4.057 | 17.710 | 0.102 | 0.174 |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| 17 | 26 W-Y2-T1-2 | 0.246 | 0.991 | 4.028 | 17.609 | 0.100 | 0.176 |
| 18 | 27 W-Y2-T1-3 | 0.249 | 0.997 | 4.004 | 17.523 | 0.101 | 0.174 |
| 19 | 28 W-Y2-T2-1 | 0.217 | 1.015 | 4.677 | 19.878 | 0.108 | 0.184 |
| 20 | 29 W-Y2-T2-2 | 0.215 | 1.011 | 4.702 | 19.965 | 0.106 | 0.188 |
| 21 | 30 W-Y2-T2-3 | 0.216 | 1.013 | 4.690 | 19.921 | 0.105 | 0.189 |
| 22 | 31 W-Y3-T0-1 | 0.280 | 0.974 | 3.479 | 15.686 | 0.102 | 0.155 |
| 23 | 32 W-Y3-T0-2 | 0.282 | 0.977 | 3.465 | 15.637 | 0.102 | 0.154 |
| 24 | 33 W-Y3-T0-3 | 0.285 | 0.971 | 3.407 | 15.436 | 0.101 | 0.153 |
| 25 | 34 W-Y3-T1-1 | 0.241 | 1.002 | 4.158 | 18.061 | 0.109 | 0.166 |
| 26 | 35 W-Y3-T1-2 | 0.245 | 1.009 | 4.118 | 17.923 | 0.106 | 0.169 |
| 27 | 36 W-Y3-T1-3 | 0.249 | 1.005 | 4.036 | 17.636 | 0.106 | 0.167 |
| 28 | 37 W-Y3-T2-1 | 0.231 | 0.999 | 4.325 | 18.645 | 0.106 | 0.175 |
| 29 | 38 W-Y3-T2-2 | 0.237 | 0.994 | 4.194 | 18.188 | 0.105 | 0.174 |
| 30 | 39 W-Y3-T2-3 | 0.235 | 0.997 | 4.243 | 18.357 | 0.105 | 0.175 |
| 31 | 40 W-Y4-T1-1 | 0.233 | 0.987 | 4.236 | 18.335 | 0.100 | 0.100 |
| 32 | 41 W-Y4-T1-2 | 0.231 | 0.988 | 4.277 | 18.478 | 0.100 | 0.101 |
| 33 | 42 W-Y4-T1-3 | 0.231 | 1.002 | 4.338 | 18.690 | 0.100 | 0.100 |
| 34 | 43 W-Y4-T2-1 | 0.225 | 1.006 | 4.471 | 19.157 | 0.100 | 0.100 |
| 35 | 44 W-Y4-T2-2 | 0.227 | 1.003 | 4.419 | 18.973 | 0.101 | 0.100 |
| 36 | 45 W-Y4-T2-3 | 0.241 | 0.989 | 4.104 | 17.872 | 0.100 | 0.101 |

**Table 3.** Total Nitrogen of Soil –CBC mixture (g C kg$^{-1}$)

| No. | Samp No. / Name | Abs(414.00) | ppm N | Digested V (mL) | Soil weight (g) | ug N / g soil | mg N / g soil |
|---|---|---|---|---|---|---|---|
| 1 | 10 Initial-1 | 1.015 | 0.207 | 6.0 | 0.1003 | 12.397 | 0.012 |
| 2 | 11 Initial-2 | 1.005 | 0.206 | 6.0 | 0.1001 | 12.365 | 0.012 |
| 3 | 12 Initial-3 | 1.009 | 0.207 | 6.0 | 0.1010 | 12.275 | 0.012 |
| 4 | 13 C-Y1-T0-1 | 1.058 | 0.212 | 6.0 | 0.1075 | 11.813 | 0.012 |
| 5 | 14 C-Y1-T0-2 | 1.055 | 0.211 | 6.0 | 0.1062 | 11.940 | 0.012 |
| 6 | 15 C-Y1-T0-3 | 1.052 | 0.211 | 6.0 | 0.1058 | 11.968 | 0.012 |
| 7 | 16 C-Y1-T1-1 | 0.959 | 0.201 | 6.0 | 0.1013 | 11.934 | 0.012 |
| 8 | 17 C-Y1-T1-2 | 0.954 | 0.201 | 6.0 | 0.1016 | 11.869 | 0.012 |
| 9 | 18 C-Y1-T1-3 | 0.958 | 0.201 | 6.0 | 0.1011 | 11.952 | 0.012 |
| 10 | 19 C-Y1-T2-1 | 0.934 | 0.199 | 6.0 | 0.1042 | 11.455 | 0.011 |
| 11 | 20 C-Y1-T2-2 | 0.936 | 0.199 | 6.0 | 0.1032 | 11.578 | 0.012 |
| 12 | 21 C-Y1-T2-3 | 0.938 | 0.199 | 6.0 | 0.1028 | 11.635 | 0.012 |
| 13 | 22 C-Y2-T0-1 | 1.250 | 0.231 | 6.0 | 0.1069 | 12.985 | 0.013 |
| 14 | 23 C-Y2-T0-2 | 1.259 | 0.232 | 6.0 | 0.1052 | 13.248 | 0.013 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 15 | 24 C-Y2-T0-3 | 1.251 | 0.231 | 6.0 | 0.1048 | 13.251 | 0.013 |
| 16 | 25 C-Y2-T1-1 | 1.197 | 0.226 | 6.0 | 0.1026 | 13.211 | 0.013 |
| 17 | 26 C-Y2-T1-2 | 1.196 | 0.226 | 6.0 | 0.1031 | 13.141 | 0.013 |
| 18 | 27 C-Y2-T1-3 | 1.199 | 0.226 | 6.0 | 0.1027 | 13.210 | 0.013 |
| 19 | 28 C-Y2-T2-1 | 1.141 | 0.220 | 6.0 | 0.1000 | 13.210 | 0.013 |
| 20 | 29 C-Y2-T2-2 | 1.143 | 0.220 | 6.0 | 0.1003 | 13.183 | 0.013 |
| 21 | 30 C-Y2-T2-3 | 1.145 | 0.221 | 6.0 | 0.1007 | 13.143 | 0.013 |
| 22 | 31 C-Y3-T0-1 | 1.011 | 0.207 | 6.0 | 0.1047 | 11.853 | 0.012 |
| 23 | 32 C-Y3-T0-2 | 1.012 | 0.207 | 6.0 | 0.1051 | 11.813 | 0.012 |
| 24 | 33 C-Y3-T0-3 | 1.015 | 0.207 | 6.0 | 0.1041 | 11.945 | 0.012 |
| 25 | 34 C-Y3-T1-1 | 1.213 | 0.228 | 6.0 | 0.1021 | 13.372 | 0.013 |
| 26 | 35 C-Y3-T1-2 | 1.219 | 0.228 | 6.0 | 0.1019 | 13.435 | 0.013 |
| 27 | 36 C-Y3-T1-3 | 1.218 | 0.228 | 6.0 | 0.1012 | 13.522 | 0.014 |
| 28 | 37 C-Y3-T2-1 | 1.233 | 0.230 | 6.0 | 0.1062 | 12.972 | 0.013 |
| 29 | 38 C-Y3-T2-2 | 1.229 | 0.229 | 6.0 | 0.1040 | 13.223 | 0.013 |
| 30 | 39 C-Y3-T2-3 | 1.228 | 0.229 | 6.0 | 0.1051 | 13.079 | 0.013 |
| 31 | 40 C-Y4-T1-1 | 0.255 | 0.958 | 5.897 | 3.757 | 1.504 | 4.007 |
| 32 | 41 C-Y4-T1-2 | 0.259 | 0.950 | 5.786 | 3.668 | 1.498 | 4.781 |
| 33 | 42 C-Y4-T1-3 | 0.258 | 0.975 | 5.925 | 3.779 | 1.529 | 4.103 |
| 34 | 43 C-Y4-T2-1 | 0.224 | 0.979 | 6.665 | 4.371 | 1.493 | 4.185 |
| 35 | 44 C-Y4-T2-2 | 0.256 | 0.972 | 5.947 | 3.797 | 1.522 | 3.789 |
| 36 | 45 C-Y4-T2-3 | 0.242 | 0.997 | 6.351 | 4.120 | 1.537 | 4.388 |

**Table 4.** Total Nitrogen of Soil –WBC mixture (g C kg$^{-1}$)

| No. | Samp No. / Name | Abs(414.00) | ppm N | Digested V (mL) | Soil weight (g) | ug N / g soil | mg N / g soil |
|---|---|---|---|---|---|---|---|
| 1 | 10 Initial-1 | 1.015 | 0.207 | 6.0 | 0.1003 | 12.397 | 0.012 |
| 2 | 11 Initial-2 | 1.005 | 0.206 | 6.0 | 0.1001 | 12.365 | 0.012 |
| 3 | 12 Initial-3 | 1.009 | 0.207 | 6.0 | 0.1010 | 12.275 | 0.012 |
| 4 | 13 W-Y1-T0-1 | 1.227 | 0.229 | 6.0 | 0.1062 | 12.937 | 0.013 |
| 5 | 14 W-Y1-T0-2 | 1.220 | 0.228 | 6.0 | 0.1051 | 13.032 | 0.013 |
| 6 | 15 W-Y1-T0-3 | 1.225 | 0.229 | 6.0 | 0.1046 | 13.123 | 0.013 |
| 7 | 16 W-Y1-T1-1 | 1.299 | 0.236 | 6.0 | 0.1078 | 13.156 | 0.013 |
| 8 | 17 W-Y1-T1-2 | 1.295 | 0.236 | 6.0 | 0.1052 | 13.458 | 0.013 |
| 9 | 18 W-Y1-T1-3 | 1.291 | 0.236 | 6.0 | 0.1061 | 13.321 | 0.013 |
| 10 | 19 W-Y1-T2-1 | 1.236 | 0.230 | 6.0 | 0.1015 | 13.591 | 0.014 |
| 11 | 20 W-Y1-T2-2 | 1.237 | 0.230 | 6.0 | 0.1012 | 13.637 | 0.014 |
| 12 | 21 W-Y1-T2-3 | 1.231 | 0.229 | 6.0 | 0.1009 | 13.641 | 0.014 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 13 | 22 W-Y2-T0-1 | 1.104 | 0.216 | 6.0 | 0.1019 | 12.740 | 0.013 |
| 14 | 23 W-Y2-T0-2 | 1.106 | 0.217 | 6.0 | 0.1009 | 12.879 | 0.013 |
| 15 | 24 W-Y2-T0-3 | 1.114 | 0.217 | 6.0 | 0.1001 | 13.031 | 0.013 |
| 16 | 25 W-Y2-T1-1 | 1.203 | 0.227 | 6.0 | 0.1018 | 13.351 | 0.013 |
| 17 | 26 W-Y2-T1-2 | 1.204 | 0.227 | 6.0 | 0.1001 | 13.584 | 0.014 |
| 18 | 27 W-Y2-T1-3 | 1.210 | 0.227 | 6.0 | 0.1009 | 13.513 | 0.014 |
| 19 | 28 W-Y2-T2-1 | 1.317 | 0.238 | 6.0 | 0.1082 | 13.210 | 0.013 |
| 20 | 29 W-Y2-T2-2 | 1.315 | 0.238 | 6.0 | 0.1061 | 13.460 | 0.013 |
| 21 | 30 W-Y2-T2-3 | 1.319 | 0.238 | 6.0 | 0.1052 | 13.599 | 0.014 |
| 22 | 31 W-Y3-T0-1 | 1.181 | 0.224 | 6.0 | 0.1015 | 13.257 | 0.013 |
| 23 | 32 W-Y3-T0-2 | 1.175 | 0.224 | 6.0 | 0.1015 | 13.221 | 0.013 |
| 24 | 33 W-Y3-T0-3 | 1.174 | 0.224 | 6.0 | 0.1009 | 13.294 | 0.013 |
| 25 | 34 W-Y3-T1-1 | 1.231 | 0.229 | 6.0 | 0.1087 | 12.662 | 0.013 |
| 26 | 35 W-Y3-T1-2 | 1.233 | 0.230 | 6.0 | 0.1061 | 12.984 | 0.013 |
| 27 | 36 W-Y3-T1-3 | 1.211 | 0.227 | 6.0 | 0.1057 | 12.905 | 0.013 |
| 28 | 37 W-Y3-T2-1 | 1.287 | 0.235 | 6.0 | 0.1063 | 13.273 | 0.013 |
| 29 | 38 W-Y3-T2-2 | 1.281 | 0.235 | 6.0 | 0.1046 | 13.453 | 0.013 |
| 30 | 39 W-Y3-T2-3 | 1.277 | 0.234 | 6.0 | 0.1052 | 13.353 | 0.013 |
| 31 | 40 W-Y4-T1-1 | 0.233 | 0.987 | 6.0 | 6.496 | 4.126 | 1.6 |
| 32 | 41 W-Y4-T1-2 | 0.231 | 0.988 | 6.0 | 6.548 | 5.001 | 1.3 |
| 33 | 42 W-Y4-T1-3 | 0.231 | 1.002 | 6.0 | 6.623 | 4.874 | 1.4 |
| 34 | 43 W-Y4-T2-1 | 0.225 | 1.006 | 6.0 | 6.790 | 5.242 | 1.3 |
| 35 | 44 W-Y4-T2-2 | 0.227 | 1.003 | 6.0 | 6.725 | 4.578 | 1.5 |
| 36 | 45 W-Y4-T2-3 | 0.241 | 0.989 | 6.0 | 6.331 | 4.322 | 1.5 |

**Table 5.** C:N rato –CBC mixture (g C kg$^{-1}$)

| **No.** | **CBC** | **g C / kg soil** | **g N / kg soil** | **C/N ratio** | SDT |
|---|---|---|---|---|---|
| 1 | Initial soil | 51.317 | 3.696 | 13.9 | 0.01 |
| 2 | 2018-CBC-T0 | 47.704 | 3.657 | 13.0 | 0.01 |
| 3 | 2019-CBC-T0 | 48.759 | 4.439 | 11.0 | 0.03 |
| 4 | 2020-CBC-T0 | 53.585 | 3.560 | 15.1 | 0.01 |
| 5 | 2021-CBC-T0 | 43.649 | 3.313 | 13.2 | 0.02 |
| 6 | 2018-CBC-T1 | 50.322 | 3.456 | 14.6 | 0.01 |
| 7 | 2019-CBC-T1 | 57.332 | 4.343 | 13.2 | 0.01 |
| 8 | 2020-CBC-T1 | 62.767 | 4.465 | 14.1 | 0.02 |
| 9 | 2021-CBC-T1 | 46.984 | 4.007 | 11.7 | 0.02 |
| 10 | 2018-CBC-T2 | 52.014 | 3.306 | 15.7 | 0.02 |
| 11 | 2019-CBC-T2 | 63.568 | 4.233 | 15.0 | 0.00 |

| | | | | | |
|---|---|---|---|---|---|
| 12 | 2020-CBC-T2 | 66.755 | 4.373 | 15.3 | 0.02 |
| 13 | 2021-CBC-T2 | 51.645 | 4.185 | 13.9 | 0.02 |

**Table 6.** C:N rato –WBC mixture

| **No.** | **WBC** | **g C / kg soil** | **g N / kg soil** | **C/N ratio** | STD |
|---|---|---|---|---|---|
| 1 | Initial soil | 51.317 | 3.696 | 13.9 | 0.01 |
| 2 | 2018-WBC-T0 | 61.075 | 4.342 | 14.1 | 0.02 |
| 3 | 2019-WBC-T0 | 58.732 | 4.068 | 14.4 | 0.03 |
| 4 | 2020-WBC-T0 | 54.204 | 4.326 | 12.5 | 0.01 |
| 5 | 2021-WBC-T0 | 44.512 | 3.646 | 13.9 | 0.02 |
| 8 | 2018-WBC-T1 | 63.306 | 4.566 | 13.9 | 0.03 |
| 9 | 2019-WBC-T1 | 64.572 | 4.457 | 14.5 | 0.02 |
| 10 | 2020-WBC-T1 | 62.233 | 4.283 | 14.5 | 0.03 |
| 11 | 2021- WBC-T1 | 54.535 | 4.126 | 13.9 | 0.02 |
| 14 | 2018-WBC-T2 | 74.373 | 4.560 | 16.3 | 0.01 |
| 15 | 2019-WBC-T2 | 72.173 | 4.643 | 15.5 | 0.04 |
| 16 | 2020-WBC-T2 | 65.610 | 4.558 | 14.4 | 0.02 |
| 17 | 2021-WBC-T2 | 55.014 | 5.242 | 13.9 | 0.02 |

**Figure 5. 23 Bacterial and fungal at Phylum level and Class level by comparison of first and third years with biochar application.**

**Table 7**. Data of microbial community on Figure Phylum (%)

| Taxon name | Soil | TO-1 | TO-3 | CBC-T2-1 | CBC-T2-3 | WBC-T2-1 | WBC-T2-3 |
|---|---|---|---|---|---|---|---|
| Alphaproteobacteria | 40.759 | 42.199 | 40.964 | 40.255 | 40.666 | 40.234 | 43.930 |
| Actinobacteria_c | 19.580 | 24.272 | 19.968 | 21.772 | 20.495 | 20.851 | 17.429 |
| Betaproteobacteria | 11.013 | 10.864 | 12.020 | 12.168 | 10.901 | 11.694 | 10.438 |
| Sphingobacteriia | 6.650 | 5.014 | 5.540 | 4.290 | 5.571 | 5.275 | 8.739 |
| Vicinamibacter_c | 5.093 | 4.050 | 6.360 | 6.463 | 6.074 | 7.040 | 5.115 |
| Gammaproteobacteria | 3.856 | 2.519 | 3.275 | 2.828 | 3.364 | 3.025 | 3.849 |
| Deltaproteobacteria | 3.837 | 3.517 | 2.978 | 3.195 | 3.514 | 3.286 | 2.117 |
| Thermoleophilia | 2.472 | 1.197 | 1.874 | 1.681 | 2.087 | 1.995 | 1.691 |
| Bacilli | 1.519 | 2.030 | 2.068 | 2.129 | 1.717 | 1.910 | 1.611 |
| Acidimicrobiia | 1.325 | 1.043 | 1.379 | 1.123 | 1.387 | 1.251 | 1.645 |
| Blastocatellia | 0.756 | 0.223 | 0.344 | 0.313 | 0.345 | 0.440 | 0.794 |
| Planctomycetia | 0.670 | 0.485 | 0.512 | 0.563 | 1.024 | 0.616 | 0.511 |
| GQ396871_c | 0.535 | 0.554 | 0.381 | 0.467 | 0.430 | 0.412 | 0.338 |
| Rubrobacteria | 0.420 | 0.621 | 0.712 | 1.100 | 0.760 | 0.65 | 0.515 |
| **Other** | 0.323 | 0.146 | 0.333 | 0.261 | 0.238 | 0.349 | 0.211 |

**Table 8.** Data of microbial community on Class (%)

| Taxon name | Soil | TO-1 | TO-3 | CBC-T2-1 | CBC-T2-3 | WBC-T2-1 | WBC-T2-3 |
|---|---|---|---|---|---|---|---|
| Alphaproteobacteria | 23.85 | 22.49 | 23.907 | 23.182 | 23.861 | 23.490 | 24.441 |
| Actinobacteria_c | 12.12 | 13.306 | 11.108 | 11.762 | 12.160 | 10.865 | 10.681 |
| Betaproteobacteria | 8.03 | 10.582 | 8.4025 | 8.152 | 8.288 | 7.829 | 10.084 |
| Sphingobacteriia | 5.59 | 3.458 | 4.7907 | 3.743 | 4.856 | 4.549 | 10.084 |
| Vicinamibacter_c | 5.08 | 5.892 | 5.9828 | 6.680 | 5.078 | 5.596 | 4.681 |
| Gammaproteobacteria | 4.21 | 4.274 | 4.3778 | 4.193 | 4.177 | 4.364 | 5.025 |
| Deltaproteobacteria | 3.69 | 3.984 | 3.5482 | 3.886 | 3.605 | 3.743 | 3.243 |
| Thermoleophilia | 3.17 | 5.809 | 3.7649 | 5.064 | 3.400 | 4.960 | 2.666 |
| Bacilli | 2.86 | 2.586 | 2.1786 | 2.273 | 2.519 | 2.477 | 1.611 |
| Acidimicrobiia | 2.29 | 2.322 | 2.5262 | 2.187 | 2.574 | 2.253 | 2.632 |
| Blastocatellia | 2.25 | 1.821 | 2.6513 | 2.077 | 2.908 | 2.815 | 1.993 |
| Planctomycetia | 2.17 | 1.554 | 1.917 | 1.710 | 1.874 | 1.827 | 2.266 |
| GQ396871_c | 2.15 | 2.945 | 3.0811 | 3.112 | 2.694 | 3.749 | 1.971 |
| Rubrobacteria | 1.96 | 2.797 | 2.5374 | 2.697 | 2.329 | 2.697 | 2.027 |
| **Other** | 1.71 | 1.381 | 1.5078 | 1.668 | 1.555 | 1.757 | 1.587 |