REDUCING NITROGEN (N) LEACHING IN AN ACIDIC SOIL BY AMENDING UREA FERTILIZER WITH RICE HUSK BIOCHAR

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DECLARATION

I hereby declare that the work embodied in this report is the result of the original research and has not been submitted for a higher degree to any universities or institutions.

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ABSTRACT

Excessive applied of N fertilizers affects plants and environment, mainly through denitrification, runoff, leaching, volatilization, resulting in waste of resources and pollution. Biochar is a by-product of the pyrolysis of biomass wastes that have a high carbon content and porous structure, and have been widely used as soil modification in agro-ecosystems. The aim of this study were to (1) Sample and characterize the selected physio-chemical properties of soil samples to be used for laboratory leaching studies (2) Characterize the selected chemical properties of rice husk biochar (3) To determine the effect of amending urea with rice husk biochar on the retention of N in the soil and the chemical properties of the selected soil. The leaching experiment was performed for 30 days and water and soil samples were collected for analysis at the end of the experiment. The urea amended with different rates rice husk biochar did not reduce the N leaching and improve the N retention in the soil compared to treatment without applications of rice husk biochar. However, the rice husk biohcar managed to improve the soil pH to near neutral.

Key words: Nitrogen, leaching, inorganic fertilizer, biochar, fertilizer, retention

MENGURANGKAN LARUT RESAP NITROGEN (N) DALAM TANAH BERASID DENGAN MENCAMPURKAN BAJA UREA DENGAN BIOCHAR SEKAM PADI.

ABSTRAK

Penggunaan baja N yang berlebihan memberi kesan kepada tumbuhan dan alam sekitar, terutamanya melalui denitrifikasi, air larian, larut lesap, volatilisasi, mengakibatkan pembaziran sumber dan pencemaran. Biochar adalah hasil sampingan daripada pirolisis sisa biojisim yang mempunyai kandungan karbon tinggi dan struktur berliang, dan telah digunakan secara meluas sebagai pengubahsuaian tanah dalam agro-ekosistem. Matlamat kajian ini adalah untuk (1) Mensampel dan mencirikan sifat fisio-kimia terpilih bagi sampel tanah yang akan digunakan untuk kajian larut lesap makmal (2) Mencirikan sifat kimia terpilih biochar sekam padi (3) Untuk menentukan kesan meminda biochar sekam padi urea pada kadar yang berbeza pada pengekalan N pada tanah dan sifat kimia tanah yang terpilih. Ujian pasu dilakukan selama 30 hari dan sampel air dan tanah dikumpul untuk dianalisis pada akhir eksperimen. Urea yang dipinda dengan kadar biochar sekam padi yang berbeza tidak mengurangkan larut lesap N dan meningkatkan pengekalan N dalam tanah berbanding rawatan tanpa penggunaan biochar sekam padi. Walau bagaimanapun, biohcar sekam padi berjaya meningkatkan pH tanah kepada hampir neutral.

Kata kunci: Nitrogen, larut lesap, baja bukan organik, biochar, baja, pegangan

TABLE OF CONTENT

DECLARATION I
ACKNOWLEDGEMENT II
ABSTRACT III
ABSTRAK IV
TABLE OF CONTENT V
LIST OF TABLE VII
LIST OF FIGURE VIII
LIST OF APPENDICES IX
LIST OF ABBREVIATIONS AND SYMBOLS X
CHAPTER 1 1
INTRODUCTION 1
1.1 Research background 1
1.2 Problem statement 5
1.3 Hypothesis 6
1.4 Scope of Study 6
1.5 Significance of Study 7
1.6 Objectives 8
CHAPTER 2 9
LITERATURE REVIEW 9
2.1 Nitrogen 9
2.1.1 Introduction of Nitrogen 10
2.1.2 Nitrogen Cycle 11
2.1.3 Classification of Nitrogen 12
2.1.4 Importance of Nitrogen in Soil plant system 13
2.1.5 Problem of Nitrogen Fertilizer 14
2.2 Urea 15
2.2.1 Production of Urea as Fertilizer in Agriculture Industry 16
2.2.2 Introduction and properties of urea 17
2.2.3 Uses of Urea 18

2.3 Leaching of Urea 18
2.4 Common management of reducing urea loss via leaching 19
2.5 Biochar 20
  2.5.1 Introduction and properties of Biochar 21
  2.5.2 Types of Biochar 22
  2.5.3 Uses of Biochar 23
2.6 Potential of amending urea with biochar in reducing urea loss via leaching ...23

CHAPTER 3 25

METHODOLOGY 25

3.1 Soil Sampling, Preparation, and Characterization 25
  3.1.1 Soil pH and Electrical Conductivity Determination 26
  3.1.2 Soil texture Determination 27
  3.1.3 Organic Matter and Organic Carbon Determination 29
  3.1.4 Cation Exchange Capacity Determination 30
  3.1.5 Nitrogen Determination 31
  3.1.6 Phosphorus Determination 32
  3.1.7 Soil Exchangeable K Determination 33
3.2 Characterization of Rice Husk Biochar 34
3.3 Laboratory Leaching Experiment 35
3.4 Post-Treatment soil analysis 37
3.5 Statistical Analysis 38

CHAPTER 4 39

RESULTS AND DISCUSSION 39

4.1 Selected Physico-Chemical Properties of Soil Samples 39
4.2 Selected Chemical Properties of Rice Husk Biochar 41
4.3 Concentration Nitrogen in Leachate over 30 Days of Leaching 42
4.4 Effect of pH, EC and Nitrogen in soil after leaching 44

CHAPTER 5 48

CONCLUSIONS AND RECOMMENDATION 48

REFERENCES 49

APPENDICES 67

LIST OF TABLE

NO		PAGE
3.1	Treatments of the incubations study	36
4.1	Selected physico-chemical properties of soil samples	39
4.2	Selected physico-chemical properties of rice husk biochar	41

LIST OF FIGURE

NO		PAGE
3.1	Leaching N from the soil using a pot	36
4.1	Concentration nitrogen in leachate over 30 days of leaching	42
4.2	Sum of leachated in the N after 30 days of leaching	43
4.3	Soil pH after 30 days of leaching	44
4.4	Soil EC after 30 days of leaching	46
4.5	Concentrations of N remained in soil after 30 days of leaching	47

LIST OF APPENDICES

NO		PAGE
APPENDIX A	Collected soil samples for analysis	67
APPENDIX B	Sample for kjedhal method during distillation	67
APPENDIX C	Water sample were collected for analysis	68
APPENDIX D	Leachate that has occurred from the soil	68

LIST OF ABBREVIATIONS AND SYMBOLS

N	Nitrogen
P	Phosphorus
K	Potassium
Na	Sodium
Mg	Magnesium
Mn	Manganese
Cu	Copper
Fe	Iron
Al	Ammonium sulfate
Si	Silicone
Zn	Zinc
N_2	Dinitrogen dioxide
NH_3	Ammonia
NH_4^+	Ammonium
N_2O	Nitrous oxide
NO	Nitric acid
NO_2	Nitrogen dioxide
NO_3^-	Nitrate
pH	Potential of hydrogen
CEC	Cation exchange capacity

AAS	Atomic absorption spectrophotometer
PPM	Part per million
X-TRAY	Energetic high-frequency electromagnetic radiation.
HCL	Hydrogen chloride
NaOH	Sodium hydroxide
(K_2SO_4).	Potassium sulphate
(NH_4OAc)	Ammonium acetate
H_2SO_4	Sulphuric acid
ºC	Celcius
ANOVA	Analysis of variance
SPSS	Statistical package for social science

CHAPTER 1

INTRODUCTION

1.1 Research background

N is an integral part of both amino acids and nucleic acids, making it the most valuable nutrient for plants. However, N supply is low in many soils, and plants are unable to use N gas N_2, despite the fact that 78.1 percent of the earth's atmosphere is N gas N_2 (Ferguson,2010). Furthermore, the use of chemical fertilizers is a procedure that is quite wasteful, because 30 to 50 percent of fertilizer N used disappeared from the washing, the primary cause of environmental problems such as eutrophication of waterways (Gragan,2003). As a result, there is a pressing need to reduce our dependence on chemical N fertilizers in favours of maximizing alternate N inputs (Ferguson,2010). Crop plants use N as a primary nutrient for growth and production. The most significant determinant of plant growth and crop production is nitrogen (N). Plants that are deficient in N have stunted growth and yellowish leaves.

When N is applied to the soil, plant growth and crop yield typically improve (Hodge,2008). Too much N, on the other hand, can cause issues in plants, humans, livestock, and the atmosphere. According (Andale,2008), best N and water management strategies will reduce the likelihood of nitrate leaching into groundwater while maintaining productive yields. It is difficult to account for observed N responses and to verify that a given output is the product of a specified N input due to the complexities of soil and crop systems (Haefner, 2005).

Urea was among the most frequently used N fertilizers on the world, and its use has increased in recent decades (Daigh et al., 2014). When urea is applied to soil, urease quickly hydrolyzes it into ammonia and carbon dioxide, resulting in N loss through to ammonia volatilization (Pan et al., 2016). Under such environmental and edaphic environments, more than 40% of added N is said to be wasted as ammonia globally (Singh et al. 2013). Urea is the most effective N fertilizer used in China's North China Plain, which is a key crop-growing region. However, in this location, excessive N fertilizer usage has been proven, and ammonia volatilization has been identified as one of the key mechanisms for N depletion, accounting for 19.4 to 24.7 N of applied N in the wheat and maize growing seasons, respectively (Ju et al., 2009). Global demand for fertilizer N is expected to grow at a rate of about 1.6 Tag (160,000 metric tons) per year, with China (18%), India (17%), and Latin America accounted for most of the increase (18%) (FAO, 2015).

However, major changes in the composition of the population in response to higher concentrations of urea which may have long-term consequences that are important to overall soil fertility and pathogen tolerance (Otto-Hanson et al., 2013). Biochar is a by-product of waste biomass pyrolysis that has a high carbon content and a porous structure, and has been extensively used as a soil modification in agro-ecosystems (Wu et al, 2019). In Japan, the rice threshing process produces around 2 million tons of rice husk per year (Kumara & Sasaki,2009). Recently, the combination pyrolysis and anaerobic digestion mechanism has gotten a lot of coverage (Sajid & Ali, H. M (2019).

Biochar is made by the pyrolysis process, which involves burning or charring biological tissues in the absence of oxygen (Mohan et al. 2006). Biochar has been shown to enhance soil properties such as chemical, physical, and biological (Yamato et al. 2006). Biochar will be made from seed leaves, woody materials, green wastes, animal manures, and agricultural wastes like rice husks. Pyrolysis can turn wastes like rice husk into biochar, which offers a variety of advantages including energy generation, sustainable waste disposal, carbon sequestration, increased soil quality, and improved plant development (Abrishamkesh, 2015). Rice husk, which accounts for 20% of the weight of rice, is a by-product of the rice milling process. However, rice husk is currently used for certain purposes such as cement additives, making fertilizer on the farm and incubating chickens. This causes the cost of rice husk to increase due to high demand (Ajiwe, 2000).

Fertilizer N that is not used by the plants tends to go out into the environment through a variety of processes including nitrification-denitrification, volatilization of ammonia (NH_3), leaching, and runoff (Vitousek, 1997). In addition to the traditional approach that is designed to improve the efficiency of use of N, such as the use of the appropriate rate and application of N depth, current techniques including management N and specific nutrients location and real-time, quick test N status of plants that do not damage, and the use of fertilizers release controlled / slow (Yan, 2008). Reduction volatilize NH_3 and loss laundering is the key to increasing the efficiency of the use of N, and N fertilizer controlled release / slow especially tend to delay their availability for the recruitment and use of plants after application or extend its availability to plants for longer than the reference fertilizer nutrients are quickly available via specific control mechanisms (Trenkel, 2010). Despite the loss of soil available N leaching is prevented by trees as providers of ecosystem services, optimization of planting time, the combination of low corn stover residue with manure N, and N application rate reduction measure its effectiveness depends on the production system (Lawrence, 2012).

Evaporation of ammonia (NH_3) is the source of the loss of nitrogen (N), the most important of the many farms that receive synthetic fertilizers based on ammonium (NH_4^+) (Sommer, 2004). In addition to the negative effects on crop productivity and profitability of farms, NH_3 emitted cause human health problems (Künzli et al., 2000) and have a negative impact on the health of natural ecosystems (Erisman et al., 2008). Among synthetic fertilizers, NH_3 emission biggest potential for urea (Bouwman and

Boumans, 2002), The cumulative loss could reach 60% N used (Sommer et al., 2004; Rochette et al., 2009a). However, the most common mitigation is the incorporation of manure into the soil because of resistance to the spread of ammoniacal N in the liquid phase and gas and retention of NH_4^+ -N in the soil particles increases when urea is placed in depth (Sommer et al., 2004).

1.2 Problem statement

Although there is several research and studies that have been carried out to reduce urea by using excess application in order to saturate the N in soil. Usage of a few types of micronutrient such as copper and zinc were also reported. However, there is a lack of research on amending urea fertilizers with rice husk rice biochar to reduce leaching of N.

1.3 Hypothesis

: Amending urea with rice husk biochar at different rates will not reduce the N, leaching in soil and improving the selected chemical properties of soil.

: Amending urea and with rice husk biochar at different rates will reduce the N, leaching in soil and improves the selected chemical properties of soil.

1.4 Scope of Study

The scope of study focuses on assessing effect of amending urea with rice husk biochar at different rates on reducing N, leading and improving the selected chemical properties of an acidic soil.

1.5 Significance of Study

Reduce waste disposal from agricultural activities. Many farmers use more fertilizer on their crops than the plants need (Hai, 2010). Several new methods of sewage treatment, such as composting and anaerobic fermentation, may be interesting, but newer and more important is the sewage sludge from urban conglomerates A.A (Manten and Ms. F. Wallien, 1979). The advantages associated with proper irrigation and fertigation including increased crop yields, improved crop quality, increased efficiency / water conservation and nutrition, reduction of energy costs and reduction of adverse effects on the environment (Shah and Das, 2012).

According to Norse (2005), save the cost of fertilizer to the role of farmers and smallholders. Despite the rapid increase in and consequent excessive fertilizers usage, particularly N fertilizers, crop yields and agricultural productivity have been slowly growing or stagnating in recent decades. Agricultural inputs such as labor, water, fertilizers, chemicals, seeds, machinery and use less energy and contributes to sustainable agricultural production and the resulting increase in profit (Yazdanifar, 2014).

According to Cast report (1975), Pollution to the environment can be reduced. However, using massive confinement manures as fertilizers is associated with high energy costs for transportation, delivery, and storage facility needs, as well as odour issues and the risk of groundwater pollution. The use of irrigation methods and systems that will improve productivity and quality is becoming more important every day that would not cause problems of drainage and salinity in the soil by applications that are more economical to use less irrigation water (Aras, 2006). According to Pierce (2010), looked at the accuracy of irrigation as a means to improve agricultural sustainability in terms of increasing the efficiency of irrigation water use irrigation and improved quality of irrigated farm environment.

1.6 Objectives

1. . To sample and characterize selected physio-chemical properties of soil sample to be used to laboratory leaching study.
2. To characterize the selected chemical properties of rice husk biochar.
3. To determine the effect of amending urea rice husk biochar at different rates on N retention at soil and selected chemical properties of soil.

CHAPTER 2

LITERATURE REVIEW

2.1 Nitrogen

N is an important nutrient, which can directly affect the growth and development of rice plants and help improve the yield and quality of rice. N is evenly degraded in most agricultural soils, and it is impossible to achieve success in agriculture. No need to use N fertilizer. In addition, the purpose of N fertilizer is to ensure a high economic return on investment by optimizing and improving the quality of crop yields. 60% is used for grain production (FAO, 2004). According to the National Statistics Department (2002), The total amount of mineral fertilizers that have been imported into Malaysia is 1.32 million tons of which the estimated value is 1.14 billion, while Malaysia has used about 677,000 tons of nitrogen-containing N fertilizers, with a total import value of N. It is estimated that the fertilizer application in Malaysia exceeds 248 million ringgits. The price of N and other fertilizers has always been a major concern for land and farmers, as more than 90% of fertilizers are used in various types of farming systems (FAO, 2004).

2.1.1 Introduction of Nitrogen

The production of crops that produce moist and temperate soils should require good nutrients such as nitrogen (N), Despite the possibility of N content in the soil may be high (Simard and Dayegamiye, 1993). There is enough mineralized organic N to produce the highest yield of modern strains. Therefore, additional N obtained from chemical fertilizers or organic resources (such as fertilizers and beans), available N in plants, N excreted from the soil or N used for fertilization, is caused by leaching and loss of soil and plant systems. The problem of losses is very sensitive to denitrification, it requires efficient and proper management of N because it is very important for a good environment and economy. By optimizing N management, agricultural yields can be increased, economic benefits can be increased, and N losses to the environment can be reduced. Nitrogen fertilizer adapts to plant N requirements by synchronizing the utilization of available N by plants and the spatiotemporal absorption of N by plants (Sharifi et al., 1999).

2.1.2 Nitrogen Cycle

Global N cycle describes the population and the most important form of N, and the process of change N to terrestrial ecosystems. Nitrogen exists in the atmosphere in the form of nitrogen (N_2), oxides (N_2O, NO and NO_2) and (NH_3). The form N can be found in water and soil, known as dissolved gas as N biogeochemical cycles found in terrestrial ecosystems the cycle can be divided into external and internal cycles (Hart et al. 1994). Increasing addition of N to the ecosystem fixation (N_2), ammonium (NH_4) and nitrate (NO_3) in water precipitation using mineral and organic fertilizers because N will disappear in the ecosystem (denitrification, NO_3 leaching and evaporation of NH_3). Including process of converting N from one chemical form to another, or transferring nitrogen between protected areas of ecosystems, including plant assimilation, using plant litter to return nitrogen to the soil, and root rotation, nitrogen mineralization and Immobilization of microorganisms. Soil removal and / or loss and return the next N between soil and atmosphere complete global N cycle.

2.1.3 Classification of Nitrogen

Nitrogen-Plants want loads of N to develop normally. Plants soak up NH_4 + (ammonium) or NO_3- from the soil (nitrate). Typical flowers include 1.5% of dry diazonium, however can variety from 0.5% for woody flowers to 5.0% for legumes. N is part of amino acids that collectively make up protein. N is likewise found in protoplasts and enzymes. After N enters the plant, it adapts and might transfer from older plant tissues to more modern plant tissues. When flowers display N deficiency, vintage leaves commonly flip yellow-inexperienced or yellow at first. As the deficiency progresses, the complete plant will flip yellow. The essential herbal supply of N in soil is natural matter.

2.1.4 Importance of Nitrogen in Soil plant system

N occupies a new position in the important parts, because it is important to consider the elements of growth, compared with other nutrients, plants need a lot of N to crops most (Zebartha et al., 2009). Plants that are not getting enough N will cause the leaves to yellow and its growth will also slow stunted. Soil that can provide enough N to crops can increase crop yields, because the use of N is more used than other nutrients. Exposure to this N mineral fertilizer indirectly produces high quality crops. The positive effects of the use of this N mineral fertilizer can be seen from the good yields for suitable crops such as wet climates, which are equivalent to potatoes (Ziadi et al., 2011). According to (Mosier, 2001), the use of N fertilizers in the agricultural system increased from 7% in 1950 to 43% in 1996. The aim is to expand output per unit to areas where the agricultural industry is thriving and productive land (Mosier, 2001). The increase in N consumption is very important because its beneficial effect on the global is around 50% and excessive consumption can have adverse effects on crop systems, groundwater, soil surface and losses (Smil, 1999).

2.1.5 Problem of Nitrogen Fertilizer

In the factors to increase profitability and productivity during the process of N fertilizer management is something important. However, fertilizer systems have resulted in between 60% and 70% of N fertilizer application being lost (Morales et al., 2000). These include the form of N fertilizer where the factors of its application method, cultivation differences, soil properties and crop system (Wang et al., 2010). Only 30% - 40% of fertilizer N used with traditional distribution methods available for growing rice and the rest suffered losses due to evaporation of ammonia, denitrification, leaching, runoff, and biological or chemical agitation (Craswell et al. 1981). The demand of N for different crops and soils is difficult to achieve because significantly different soil and farm conditions (Zebarthb et al., 2009). Dry and semi-dry environment, soil N mineralization consisting of crop residues and other organic materials including mineral deposits N from previous crop. In addition, areas with humid climates will cause mineralization N losses such as autumn and winter (Zebarth et al., 2009).

2.2 Urea

In Chinese agriculture, Urea is used as one of the traditional chemical N fertilizers which accounts for 67% of total nitrogen (Zhang et al., 2013). Reducing the release of N and maintaining a plant-based N diet will be the focus of China's biochar technology. In agriculture (Pan et al., 2015), charcoal can react with urea N to form urea, and changing biochar can help reduce N emissions in agricultural soils fertilized with chemical NH_4Cl (Wen et al., 2017). Increased ammonia secretion on the biochar surface will slow down the N release process when heated (Manikandan and Subramanian 2013). Producing complex biochar fertilizers that can be used in environments requires a mechanical process using bentonite and biochar (Joseph et al., 2013). Mix biochar, clay and chemicals, but convert them into steam to form solid particulate compounds of biochar fertilizer and mineral compounds (Pan et al., 2017).

2.2.1 Production of Urea as Fertilizer in Agriculture Industry

Urea is regularly applied to topsoil in durum wheat and durum wheat production until spring. In spring wheat and durum production, an unmarried preplant N utility is conducted (Franzen, 2011). Urea is implemented to a few fields in past due fall earlier than soil freeze-up, generally in past due October. Urea is likewise implemented with inside the spring to different fields previous to seeding in April or May, and sometimes, however now no longer as regularly, implemented straight away after seeding at the soil floor. Although floor utility of urea not encouraged with the aid of using University Extension specialists, it's far nonetheless used by an encouraged with the aid of using University Extension specialists, it's far nonetheless used by a massive range of growers. Surface urea, each with inside the fall and with inside the spring is situation to N loss thru urease interest and ammonia volatilization. In addition, fall or early spring utility of urea is regularly situation to nitrification, observed with the aid of using nitrate leaching or denitrification (Franzen,2011). Immediately previous to flooding, sixty-five to 100% of the whole N fertilizer requirement (i.e., generally one zero one to 168 kg N ha−1) is normally implemented as urea directly to a dry soil and the flood hooked up as expeditiously as possible (Norman et al., 2003). The flood changed into powerful urea into the soil and forestalls the evaporation of ammonia (Savin et al., 2007). Significant uptake of urea ammonia can occur with inside the location 5 to fourteen days earlier than the flood occasion and significantly.

2.2.2 Introduction and properties of urea

The current global population, which has reached about 7 billion and could reach 9.9 billion by 2050, it requires a change in cropping systems and food supplies (Azeem, 2014). N fertilizer will disappear through evaporation, washing, and runoff with the agricultural management system. According to data records, about 45-55% of full N fertilizers implemented with the help of farmers become one reason due to low N fertilizer application performance (Yang, 2012). This poses an unavoidable problem to the environment as it can cause water pollution and large-scale release of harmful gases (Yan,2008). In addition, software for cutting urea fertilization more expensive than straight and reduce the profitability of growing cotton (Yang et al., 2012). Besides that's, it is very important to optimize the use of N fertilizer by knowing the appropriate rate of N to the crop or soil and reducing pollution to the environment. Urea fertilizer is produced and operated to facilitate management, reduce costs and obtain better quality agricultural products (Yang et al., 2012b).

2.2.3 Uses of Urea

Ammonia fertilizers, especially urea, are widely used by many farmers due to their low price and extensive N content per unit (United States Department of Agriculture, 2011). In addition, they are easy to manufacture, store and transport. Distribution and manipulation (Hauck 1984). Urea is also used to make melamine where it is used in the manufacture of melamine-methanol resin because it forms an important resin and the use of urea is also increasing in reducing air pollution from diesel engines such as cars, buses and trucks The Essential Chemical Industry – online (2017). The use of urea in the manufacture of fertilizers is an important factor but at the same time urea is also used to make urea-formaldehyde resins (Britannica, 2021).

2.3 Leaching of Urea

Loss of N as a result of leaching stems from various sources of N used in the soil (Bhopal et al., 2017). The use of N fertilizer in the early stages makes the natural process high nitrate. The study found a good nitrate leaching rate in the first 3 days and the directional flow will decrease until the end of the incubation period. The speed and quantity of nitrate leaching out of N fertilizer varies depending on the particular period (Kundu et al., 2018). Improved nutritional and crop yields depend on more concentrated fertilizers (Dong et al., 2016). Increased water utilization rate of production systems with slow cathartic capacity and able to replenish accessible nutrients in the soil (Zhang et al., 2017).

2.4 Common management of reducing urea loss via leaching

Among them, the improvement in the efficiency of using N is the key and has been extensively studied. Usually**,** N fertilizer that is no longer used by crops will be channelled to the sewer through various processes such as leaching, runoff, ammonia volatilization (NH_3) and nitrification-denitrification (Vitousek, 2002). Various traditional methods or approaches can be done to improve the efficiency of N application such as appropriate dosage, deep application of N. In addition, N management is practiced faster, does not damage crops, testing at specific locations and fertilizer application with controlled release (Xiang, 2008). The latter method is the fastest and easiest method to do to reduce fertilizer loss thus increasing efficiency (Xu-sheng, 1998). The addition of the N aims to increase the absorption of fertilizer N and set the volatilization effects after use. The use of steel instead of urea, urease inhibitors, controlled release fertilizer, fertilizer use in agriculture, irrigation and the addition of the mixture changes (Pan, 2016). According to Peng et (2011), Controlled release can reduce the leaching losses of N fertilizer application by using chemical or physical technique methods (Ni, 2011).

2.5 Biochar

Biochar can be classified as solid as the product must undergo a process of decomposition known as biomass thermal in an environment of low oxygen content (Lehmann et al, 2015). During the pyrolysis process, biochar is produced using carbonated materials with organic compounds from biological waste at a temperature of 350 to 600 ° C. Carbon will be converted to be more stable and have a wider surface to help retain nutrients especially N in the soil and solutions (Bian et al., 2016).

2.5.1 Introduction and properties of Biochar

The N retention capacity of biochar can vary depending on the raw material and the pyrolysis temperature used to produce the biochar (Li et al., 2018b). People recommend the use of a developed pyrolysis system with a constant high carbon content and nano-scale porosity, as well as the ability to store water and nutrients to produce agricultural biological waste (Pan et al., 2017). The utilization rate of P, K and Si increases, but the utilization rate of potentially toxic metals decreases, and chemicals or antibiotics are eliminated. These bio machines are usually used to improve soil, and the dosage is usually to increase soil fertility requires 20 to 50 t ha-1, as well as to fix heavy metals and improve carbon sequestration in the soil (Bian et al., 2014). Consumption of large amounts of biochar on farms using biological waste processing methods cannot provide positive returns to agriculture. (Claire et al., 2014). Instead, a small number of high-functionality products based on biochar may be a cheap but efficient solution, such as a new type of nanocarbon used to combat metal soil pollution (Li et al., 2019). A study by Joseph (2013), concluded the advent of biochar based BCF (compound fertilizer) technology, which greatly improves agronomic nutrition efficiency and stimulates plant growth, this may change the mineral fertilization paradigm of green agriculture. At the same time, the use of chemical fertilizers and greenhouse gas emissions have been reduced (Qian et al., 2017).

2.5.2 Types of Biochar

Biochar, carbon gas, which is obtained by outlining the terms of biomass as carbon in oxygen restricted environment (K.Pittman et al, 2014). Because an important role in the carbon, it has attracted more attention. Alienate, dispose of organic and inorganic pollutants and improve soil fertility (J. Liang et al, 2015). However, because of the nature of the raw material and the characteristics of biomass, biochar adsorption of heavy metals in relation to the nature of the pyrolysis biochar where circumstances such as the type of reactor and the pyrolysis temperature (K. Klasson et al, 2011). Previous studies have shown that when the pyrolysis temperature increases, pH, ash and carbon content, surface and pore volume increased biochar, while the ratio of biochar, H / C and O / C, cation exchange capacity (CEC), the average pore diameter is reduced. (P. Brooks et al 2014). Stalks of grain (without leaves), rice hulls, corn stalks (without leaves), branches of peach, rice walnut, Adam, sawdust white wood and sawdust are all from rural China (Wang Yang et al, 2017).

2.5.3 Uses of Biochar

Increased use of biochar in livestock-related articles on the use of biochar on livestock and poultry. According to Gerlach & Schmidt (2012), The use of biochar is used as a change in agricultural land in a lot of use of biochar, stick to the pores and surface of biochar, in many cases it has the ability to move the internal immune system of plants. Resistance capacity will increase to any pathogen (Elad et al., 2011). In addition, the construction industry also uses dry air. Due to the condensation of air in the outer walls, it can cause respiratory diseases and allergies as well as moisture which can lead to the spread of mold (Schmidt, 2013). The production of biogas at the same time will release carbon dioxide and ammonia can be reduced (Inthapanya et al., 2012).

2.6 Potential of amending urea with biochar in reducing urea loss via leaching

According to Sanchita Mandal (2016) found that adding biochar to the soil to reduce evaporation of about 70% NH_3.Perform reduction to with N leaching after addition to biochar due to NH_4^+ adsorption thus due to higher N immobilization (Congreves, 2016). High financial costs lead to limited use of newly produced fertilizers (Zheng, 2013). These steels known as steel lost control (LCF) is effective in reducing emissions reduction and NH_3 volatilization (Zhou, 2016). Addition of modified attapulgite to electron ray exposure for oxidant and hydrothermal processing (Cai, 2014).

Although it was found that trees as providers of ecosystem services prevent losses through leaching of N from soils, optimize the tillage time, combine low-quality corn stubble residues with N fertilizers and reduce the amount of N applied (Tully, 2012). The overall effectiveness of these measures depends on the production system. The lack of polymer coating material requirements in LCF during the production process facilitates the application of one field and provides environmentally friendly properties as a natural degradation so that long -term use can be made. Several factors that can reduce N loss such as plant biological properties, crop yield, soil physical and chemical properties and water resistance (Ma, 2019).

CHAPTER 3

METHODOLOGY

3.1 Soil Sampling, Preparation, and Characterization

In this study, the soil samples were sampled at 0-30 cm from an uncultivated land in Agro Techno Park of University Malaysia Kelantan Jeli Campus, Malaysia which has not been cultivated since 2007. For initial soil characterization, the collected soil samples were air dried, crushed, and sieved to pass through a 2 mm sieve. By using a digital pH meter, soil pH were measured in a ratio of 1: 10 (soil: water) (Peech, 1965). Hydrometer method were used to determine the soil texture (Jones, 2001) while loss-on ignition method were used to measure organic matter content (OM) and total organic carbon (TOC) (Tan, 2005). The Kjeldahl method will be applied in order to determine the total N (Bremner, 1965). Besides, double acid method which described by Mehlich (1953) were used to extract soil available P and exchangeable K.

Afterwards, an Atomic Absorption Spectrophotometer (AAS) were used to determine those cations (Analyst 800, Perkin Elmer, Norwalk, USA), while soil available P were measured by using molybdenum blue method (Murphy and Riley, 1962). The developing of blue colour were analysed by UV-Vis spectrometer at 882 nm wavelengths spectrometer (Thermo Scientific Genesys 20, USA). The method described by Cotteine (1980), which an ammonium acetate leaching method were applied in order to measure soil cation exchange capacity (CEC). The exchangeable NH_4^+ and available NO_3^- were extracted by using a method described by Keeney and Nelson (1982), after which the ions were determined via steam distillation (Tan, 2005). The detailed procedures of each analysis are described as follow:

3.1.1 Soil pH and Electrical Conductivity Determination

Soil pH and electrical conductivity were measured by using soil water method. Firstly, 5 g of air-dried soil were added into 100 mL conical flask. Next, 50 mL of distilled water was added and shake it at 180 rpm for 15 minutes. After that, the mixture was left to stand overnight (24h). Then, the soil pH was measured after 24 hours settling time by using pH meter. After determination of soil pH, the suspension was filled to pass through Whatman filter paper No. 2 and the filtrate was used to measure the electrical conductivity by using EC meter.

3.1.2 Soil texture Determination

The soil texture was determined by using hydrometer method. In this method, the texture of the soil was determined by measuring total sand (2.0 - 0.05 mm), silt (0.05 - 0.002 mm), and clay (<0.002 mm). 50 g of soil sample were added with 10 mL sodium metaphosphate and 100 mL water before blended continuously for 15 minutes. After 15 minutes, the soil suspension was transferred into a 1000 mL measuring cylinder without leaving any soil left. Next, distilled water was added until the volume in the cylinder reaches 1130 mL. Then, the mixtures were stirred by using stirring rod to ensure thorough mixing of sediments in the suspension. A hydrometer was placed carefully into a suspension and exactly after 40 seconds after the stirring has stopped, and the reading of the meniscus on the hydrometer stem were recorded. The hydrometer was rinsed and cleaned dry. Afterwards, the suspension was stirred on more time and the analysis of the 40 seconds reading will be repeated. The hydrometer will be rinsed and cleaned dry once again. The suspension was stirred thoroughly again and the third hydrometer reading were taken after 2 hours of settling time by following the previous reading method. The amount of silt and clay respectively were represented by the given formula where x represents first reading, y for second reading and z for third reading.

The basic principle of the calculations is:

% sand +% silt +% clay = 100%

(x + y) / 2 = a

40s reading : % (silt + clay) = (a/50) × 100 = b

% sand = 100 – b = c

2 hours reading: % clay = (x/50) × 100 = y

% silt = 100 - c - y

3.1.3 Organic Matter and Organic Carbon Determination

Total organic matter and organic carbon were measured by using dry combustion method (loss on ignition method). Firstly, the soil sample was oven-dried for 24 hours at 60 ^{0}C. Then, the sample was left to cool in a desiccator. Afterwards, the initial weight of the porcelain crucible was determined. Next, 5 g of soil sample were placed into the porcelain crucible and then, the weight of porcelain crucible plus soil sample were measured. After that, a sample was placed into a muffle furnace and initially ashed for one hour at 300 ^{0}C. Later, the temperature was raised to 550 ^{0}c and the ashing will continue to operate for 8 hours to let the soil sample to cool down before weighing. Subsequently, the weight of the sample and crucible after ashing were determined. The organic matter and total carbon were determined by using the following formula:

$$\text{Organic matter (\%)} = \frac{\text{(Initial weight of sample and crucible (g)} - \text{Final weight of sample and crucible (g))}}{\text{Initial weight of sample (g)}} \times 100$$

$$\text{Total Carbon} = \text{\% Organic matter} \times 0.58$$

3.1.4 Cation Exchange Capacity Determination

The cation exchange capacity (CEC) of the soil was determined by using ammonium acetate (leaching method). Firstly, 10 g of soil were weighed and will be placed into the conical flask. Then, 100 mL of 1M ammonium acetate (NH_4OAc) was added into soil and were shake at 180 rpm for 5 hours. After 5 hours, the soil was filtered to pass through Whatman filer paper No. 2, and then the filtrates were discarded. Next, the soil was washed with 20 mL of 95% ethanol and filtered again where ethanol was discarded after collection. Later, the soil was filtered with 100 mL of 0.1 M potassium sulphate (K_2SO_4). The filtrates were collected and make the volume of volumetric flask up to 100 mL. Afterwards, 10 mL of the sample was pipetted into the distillation apparatus. Then, 10 mL of 40% sodium hydroxide (NaOH) were added into the same beaker. The sample was distilled, and the distillate was collected in 10 mL of 2% boric acid indicator solution. During the distillation process, the reddish-purple colour of boric acid changed from to green colour. When twice of the original volume (20 mL) was obtained, the 100 mL conical flask containing the distillate was removed from the distillation apparatus. After that, the distillate was titrated against 0.01 M HCL until the green colour changed to reddish purple. This gives the CEC in cmol kg^{-1} and the CEC of the soil were calculated by given formula:

Cation exchange capacity of soil (cmol kg^{-1})

$$= \frac{[\text{Titrate value (mL)} \times \text{concentration of acid used} \times 100 \times 10 \times 1000]}{10}$$

3.1.5 Nitrogen Determination

N content in soil was determined by using Kjeldahl method or also known as wet oxidation method (Kjeltec 8200). Firstly, 5 g of air-dried soil were weighed and placed into the digestion tube. 5 mL of sulphuric acid (H_2SO_4) was added and then, followed by 1 g Kjeldahl catalyst tablet into the digestion tube. The digestion tube was arranged in Kjeldahl digestion block and was digested for 3 hours at 400 ^{0}C until the sample become colourless. After 3 hours, the sample was left to cool down for 15 minutes before adding 30 mL of distilled water. The sample was transferred into a 100 mL conical flask after it was cooled down, and the volumes were made to fill up to 100 mL. Next, 10 mL of the extract were pipetted into the distillation apparatus, and followed by 10 mL of 40% NaOH. The sample was distilled for 3 minutes and was collected in 10 mL of 25% boric acid indicator solution. Then, the reddish-purple colour of boric acid changed to green colour. After that, the sample was titrated against 0.01 M H_2SO_4 till the colour changed from green to reddish purple. The calculation for percentage of N in soil was as follows:

$$N\ (\%) = [\ (V\text{-}B) \times M \times R \times 14.01\ /\ Wt \times 1000] \times 100$$

Where,

V = Volume of 0.01 M H_2SO_4 or H_2SO_4 titrated for the sample (mL)

B = Blank titration volume (mL)

M = Molarity of H_2SO_4 solution

14.01 = Atomic weight for N

R = Ratio between total volume of the extract and the extract volume used for distillation

Wt = Weight of the sample (g)

3.1.6 Phosphorus Determination

The soil available P was extracted by using Double Acid Mehlich method. The soil available P was extracted by using double acid Method (Double acid Mehlich method. Firstly, 5 g of soil sample were placed into the 250 mL conical flask. 20 mL double acid (0.05 M HCL + 0.025 M H_2SO_4) was added into the sample and shake it at 180 rpm for 10 minutes. Afterwards, the supernatant was filtered by using Whatman filter paper No. 2. Next, the 8 mL of reagent B were pipetted into 50 mL volumetric flask. After that, 0.1 to 5 mL soil extract were added slowly while the light blue colour development were absorbed. Then, 50 mL of distilled water was added once the solution colour turned blue. Subsequently, the sample was pipetted into cuvette. UV-Vis reading at wavelength of 882 nm were recorded and subjected for calculation as follow to obtain the soil available P.

$$\text{Soil available P} = \text{UV-Vis reading} + \frac{20}{5} + \frac{50\ \text{mL}}{\text{volume of extractant}} \text{ x } \text{Dilution factor}$$

3.1.7 Soil Exchangeable K Determination

The soil exchangeable K was extracted by using Mehlich No. 1 Double Acid method. Firstly, 10 g of soil sample were placed into the 250 mL conical flask. Then, 40 mL double acid (0.05 M HCL + 0.025 M H_2SO_4) were added into the sample and shake it at 180 rpm for 15 minutes. Next, the supernatant was filtered by using Whatman filter paper No. 2. Afterwards, the extract absorbance was determined by using an atomic absorption spectrophotometer

(AAS) and the reading was recorded. The soil exchangeable cations were subjected to the formulation below:

cation (ppm)

$$\text{Soil exchangeable} = \text{ASS reading (ppm)} + \frac{\text{Volume of extractant (mL)}}{\text{Weight of soil sample (g)}}$$

3.2 Characterization of Rice Husk Biochar

The biochar was obtained from the postgraduate student. The biochar was produced by using a 200 L cylindrical kiln with the burning time of 4–6 hours, with temperature ranging from 300–400 ^{o}C and left for cooling for 12 h. Activation of biochar was carried out by soaking the biochar with 5% chicken slurry for 7 days, which later was dried and stored in a big container for further use.

The studies that have been done to find out more thoroughly about biochar are similar to the information on soil above. In addition, a scanning electron microscope associated with energy scattering x-ray spectroscopic analysis (SEM-EDX JEOL JSM 6400) for micro-analysis. It was carried out to analyze the surface area morphological information of rice straw and rice husk biochar.

3.3 Laboratory Leaching Experiment

A laboratory leaching experiment was conducted in a research complex at University Malaysia Kelantan, Malaysia. Pots (15 cm in height, 13 cm in width, and 13 cm in diameter) were filled with 600 g of soil (from 2 mm bulked Bekenu Series soil sample). Amended organic matter and chemical fertilizers will be mixed once together with the soil before the leaching experiment is carried out. The combinations of treatments were based on the treatments tested in the field trial. The rates of the P fertilizers (TSP and ERP), pineapple leaf residues, and the biochar that was used in this study were 60 kg P_2O_5 ha^{-1}, 10 t ha^{-1}, and 20 t ha^{-1}, respectively. These rates were based on the standard recommendation for maize cultivation (MARDI, 1993, Zhang *et al.*, 2012; John *et al.*, 2013). Based on these recommendations, 5 g of TSP, 8.24 g of ERP, 11.2 g of biochar, and 11.2 g compost per pot containing 600 g of soil were used. The treatments were arranged in a completely randomized design with three replications (Table 3.1). Treatments evaluated in this leaching experiment were summarized as follows:

Table 3.1: Treatments of the incubation study

Treatments	Descriptions
T0	Soil only
T1	Soil + 5 gram UREA
T2	Soil + 5 gram UREA + 1.5 Gram Rice husk biochar
T3	Soil + 5 gram UREA + 3.0 Gram Rice husk biochar
T4	Soil + 5 gram UREA + 4.5 Gram Rice husk biochar
T5	Soil + 5 gram UREA + 6.0 Gram Rice husk biochar

Figure 3.1: Leaching N from the soil using a pot

3.4 Post-Treatment soil analysis

Water is sprayed into all pots containing soil so that it is leaching through the accumulated soluble water to determine the N missing from the soil. The total volume of water watered is based on the total volume of rainy days for 30 days. Water will be poured into each pot holding soil to cause leaching, and water samples will be taken to determine the quantity of N lost from the soil. The total amount of water utilised is calculated using rainy days during a 30-day period. The average monthly rainfall is used based on rainfall data for 5 years obtained from the Malaysian Meteorological Department. Leachate was collected for analysis every 3 days for N, pH. After that, soil samples were collected after 30 days of leaching occurred. All soil samples were dried and analyzed to determine the total pH, exchangeable acidity, total N through the standard procedure set out earlier in chapter 3.

3.5 Statistical Analysis

The experiment was arranged in a completely randomized design with three replicates. SPSS software version 24.0 (SPSS Inc, US) was used to determine the statistical analysis for all the data. The effect of different biochar supplementation rates on all treatments was based on one -way analysis of variance (ANOVA). Significant differences among treatments were separated by using Turkey’s HSD test and considered significant at P ≤0.05.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Selected Physico-Chemical Properties of Soil Samples

Table 4.1 Selected physico-chemical properties of soil samples

Property	**Value obtained**
Soil textural class	Sandy loam
pH	4
Electrical conductivity (μ m^{-1})	13.33
Soil organic matter (%)	5.87
Soil total carbon (%)	3.4
Soil total N (%)	0.18
Available P (ppm)	4.5
Exchangeable K (ppm)	6.67

The selected physio-chemical properties of the acid soil were shown in table 4.1. The soil texture of the soil was sandy loam with a pH of 4. The high concentration of Al and Fe in the soil led to the soil's low pH (Ch’ng, 2016). Micronutrients such as Fe, Cu, Mn, and Zn are typically accessible at pH levels ranging from 4 to 6. Because these micronutrients are strongly bonded to the soil at high pH levels, they are more accessible at low pH levels (Halvin et al., 2006). The soil organic matter (SOM) content for the soil samples was 5.87, which considers having high organic content. The high concentrations of Fe and Al in the soil will result in poor P availability (McBride & Martinez, 2000). The soil contains relatives low N and this could be due to the immobilized and fixed of N in the soil.

4.2 Selected Chemical Properties of Rice Husk Biochar

Table 4.2 Selected physico-chemical properties of rice husk biochar

Property	**Value obtained**
pH (water)	9.1
CEC (cmol kg^{-1})	66.6
Total N (%)	0.33
Available P (mg kg^{-1})	14.3
Exchangeable Ca (mg kg^{-1})	1048
Exchangeable Mg (mg kg^{-1})	508
Exchangeable K (mg kg^{-1})	4925
Exchangeable Na (mg kg^{-1})	256

The selected physico chemical property of rice husk biochar is shown in Table 4.2. Biochar is a by-product of waste biomass pyrolysis that has high C content and a porous structure, and has been extensively used as a soil modification in agro-ecosystems (Wu et al, 2019). According to the research by Busscher et al., (2010), the pH of rice husk biochar was 9.1 which indicate alkaline properties. Alkaline biochar that have been applied to acidic soils can help to raise the pH of the soil and change nutrient bioavailability (Raboin et al., 2016). The high pH recorded in rice husk biochar was supported by the high Ca and Mg contents in the rice husk biochar.

4.3 Concentration Nitrogen in Leachate over 30 Days of Leaching

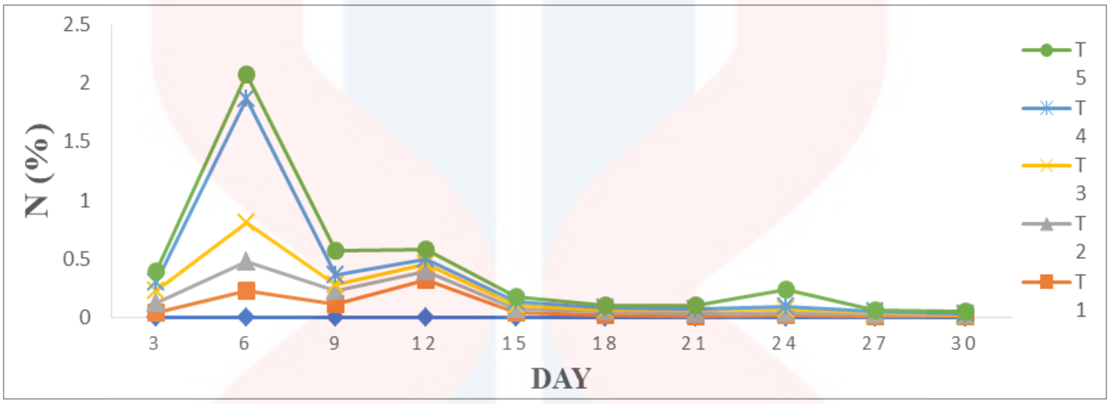

Figure 4.1 Concentration Nitrogen in leachate over 30 days of leaching

Figure 4.1 shows the effect of rice husk biochar on N leaching for over 30 days. The N leaching started in day 3 for T1 – T5. The N leaching was high in treatment with biochar (T2 – T5) compared to T1. This could be due to the dissolution of the inherent N contained in the biochar. The nitrogen retention capacity of biochar can vary depending on the raw material and the pyrolysis temperature used to produce the biochar (Li et al., 2018b).

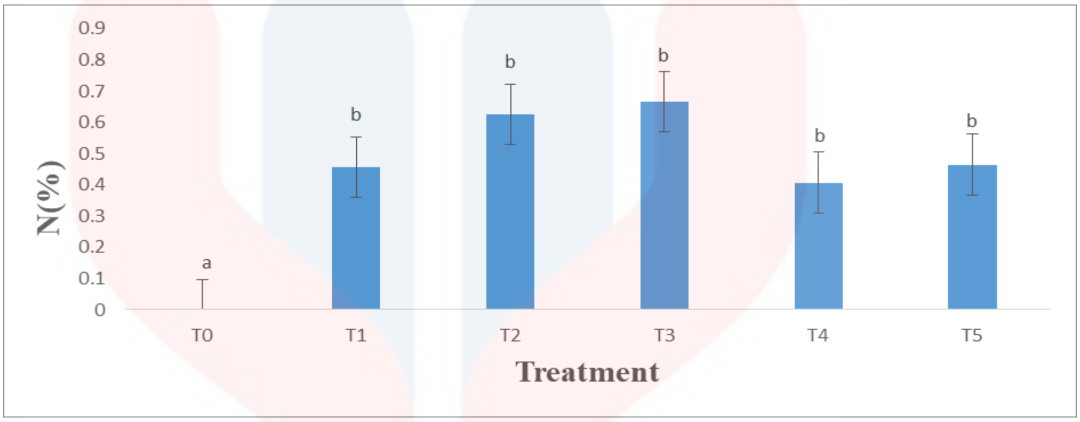

Figure 4.2 Sum of leachated in the N after 30 days of leaching

*Mean between columns with different letter (s) indicate significant difference between treatments by Tukey's test at p≤0.05

Figure 4.2 shows the effect of treatment on the sum of leachate in the N after 30 days of leaching. Based on the graph, T1, T2, T3, T4 and T5 did not have significant different in terms of N concentration in the leachate. The indicates that different rates of rice husk biochar did not exert effect on the retention of N on the surface of biochar. This could be due the lower charring temperature of the biochar during production. This is because high temperatures of charring process will improve the surface area and pure volume of the biochar which will increase the O− and COO− functional groups to for cations exchange and chelation process. During the pyrolysis process, biochar is produced using carbonated materials with organic compounds from biological waste at a temperature of 350 to 600 ° C. Carbon will be converted to be more stable and have a wider surface to help retain nutrients especially nitrogen in the soil and solutions (Bian et al., 2016). Previous studies have shown that when the pyrolysis temperature increases, pH, ash and carbon content, surface and pore volume biochar, while the ratio of biochar, H / C and O / C, cation exchange capacity (CEC), the average pore diameter is reduced (Chen et al., 2014).

4.4 Effect of pH, EC and Nitrogen in soil after leaching

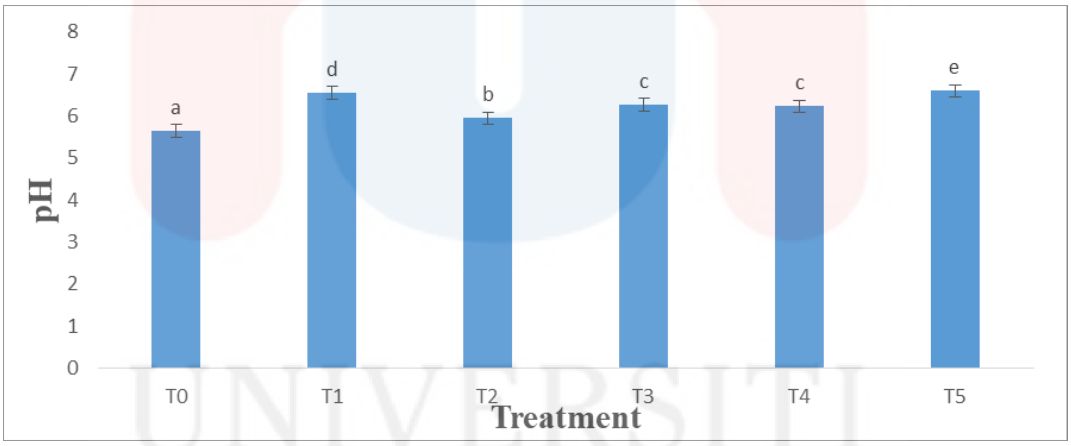

Figure 4.3 Soil pH after 30 days of leaching

*Mean between columns with different letter (s) indicate significant difference between treatments by Tukey's test at $p \leq 0.05$

The effect of rice husk biochar on the soil pH after 30 days of leaching is shown in Figure 4.3. The treatments of urea amended with rice husk biochar (T2 – T5) decreased the soil acidity by improving the soil pH to neutral compared to T0 (soil only). The soil pH was increased basically due to the initial pH of the rice husk biochar which was 9.1 (Table 4.2). Besides, the increased soil pH was also due to the precipitation of Ca by the rice husk biochar (Voutsa et al., 1996). The high buffering capacity of the biochar also explains the increase of soil pH in those treatments amended with rice husk biochar. The increase of soil pH in T1 could be due to the leaching of those acidic cations such as H^+ that contributes to the acidity of the soil. Biochar is in alkaline nature which can increase the pH of acidic soils. The alkaline nature in several biochar can be a major source to improve crop production in most acidic soils and highly weathered soils (Yeboah et al., 2009)

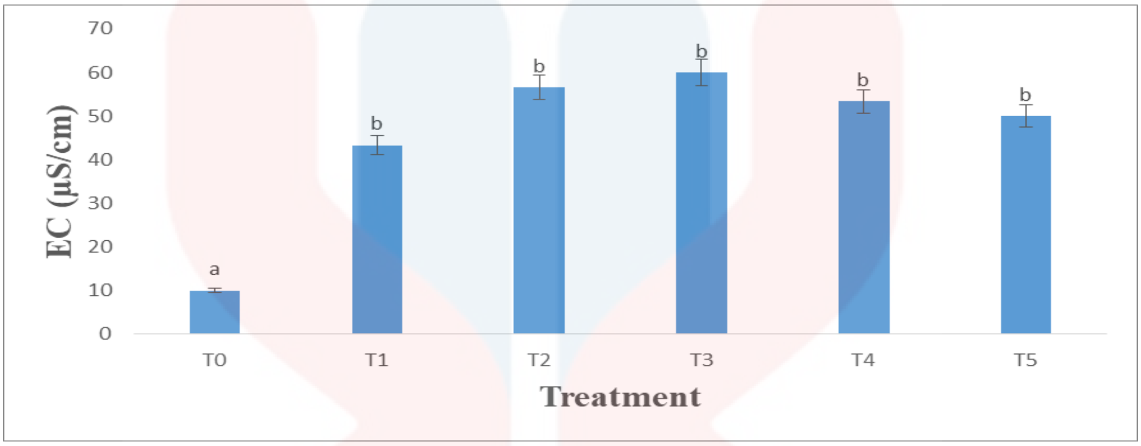

Figure 4.4 Soil EC after 30 days of leaching

*Mean between columns with different letter (s) indicate significant difference between treatments by Tukey's test at p≤0.05.

The effect of rice husk biochar in soil EC after 30 days of leaching is shown in Figure 4.4. The EC in the soil increased after 30 days of leaching in treatments with the applied of rice husk biochar (T2 – T5). This was due to the inherent Na contains in the rice husk biochar (Table 4.2) that increased the salinity of the soil. Significant increases in EC values were also influenced by the addition of basic cations from biochar implemented into the soil (Chintala et al., 2014). However, the salinity concentrations were still in the range of 0 – 2 µS/cm which indicates optimum soil salinity level for optimum plant growth. A study by Ghorbani and Amirahmadi (2018), the use of rice husk biochar increases soil salinity with increasing EC value in the soil.

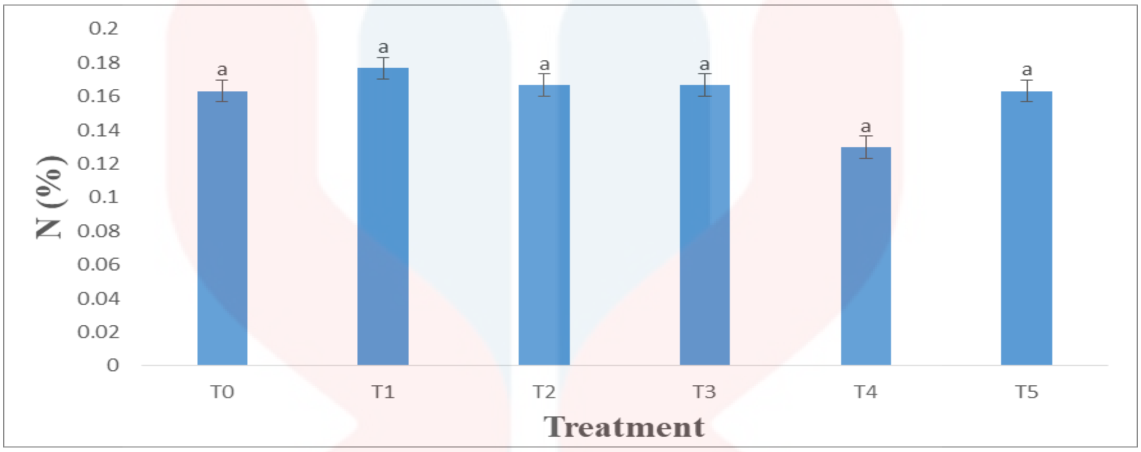

Figure 4.5 Concentrations of N remained in soil after 30 days of leaching

*Mean between columns with different letter (s) indicate significant difference between treatments by Tukey's test at $p \leq 0.05$.

The N concentration retained in the soil after leaching for 30 days is shown in Figure 4.5. The N content in T0 – T5 was not significance different. This indicates the urea amended with different rates of rice husk biochar did not reduce the N leaching and improve the retention N in the soil. This could be due to inefficient biochar in chelation the N on its surface area that prevents N from leaching (Laird et al., 2010). As a result, this will result in a slow loss of cations and reduce the risk of nutrient leaching when nutrients are absorbed to the biochar surface (Laird et al., 2010a; Beck et al., 2011). This was mainly due to the low charring temperature (<300°C) during the biochar production that failed to increase the surface area and functional groups exchange sites for N chelation.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATION

As a conclusion, the urea amended with different rates rice husk biochar did improve the N retention by reducing the N leaching rates in the soil compared to treatment without applications of rice husk biochar. However, the rice husk biochar managed to improve the soil pH to near neutral. The recommendation for future research is different charring temperature of the biochar could be evaluated/assessed to determine their effectiveness in reducing the N leaching and improve N retention in the soil.

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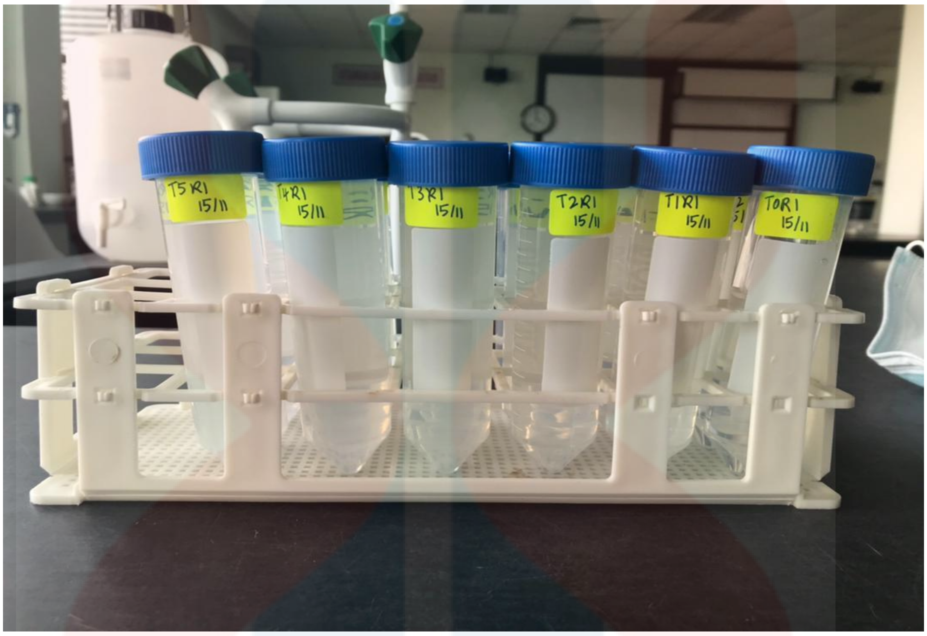
APPENDICES

Appendix A: Collected soil samples for analysis

Appendix B: Sample for kjedhal method during distillation.



Appendix C: Water sample were collected for analysis

Appendix D: Leachate that has occurred from the soil