

**Effects of Rice and Sorghum-straw Derived Biochars on Selected Plants
Grown on Spent Oil-Contaminated Soil**

BY

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MAY, 2021

CERTIFICATION

I certify that this thesis was conducted by FOLARIN, Olamide Omolafe under my supervision and approved as meeting the requirement of the Department of Plant Biology, University of Ilorin, Nigeria for the award of Doctor of Philosophy (Ph.D) degree in Plant Biology.

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DEDICATION

This research work is dedicated to Almighty God, the omniscient.

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ABSTRACT

The increased presence of Heavy Metals (HMs) in soil has been a great public health and environmental concerns in developing countries. Spent oils that are discharged indiscriminately into the environment or used as herbicides have been found to contribute to the release of HMs into the soil. The use of biochar as an amendment agent in Spent Oil-contaminated Soil (SOS) has been found to be a simple, cheap, and sustainable HMs remediation technology. This study aimed at investigating the potential of Rice and Sorghum Straw-derived Biochars (RSSB) on HMs mobility in *Tridax procumbens*, *Zea mays*, *Tithonia diversifolia* and *Pennisetum glaucum* grown in SOS. The objectives of the study were to determine the: (i) physicochemical properties of RSSB; (ii) functional properties of RSSB; (iii) physicochemical properties and HMs contents of SOS; (iv) growth potential of the selected plants in SOS; (v) mobility of HMs in the selected plants; and (vi) phytoextraction potentials of the selected plants.

Biochars derived from rice and sorghum straws by slow pyrolysis were characterized for physicochemical and functional properties using standard methods. Composite soil was spiked with spent oil (5% v/w), potted and amended with different concentrations (0, 1, 2 and 3% w/w) of biochar. The soil was incubated for 30 days and physicochemical properties were determined using standard methods. Seeds of the selected plants were sown in the treated soil and their growth attributes were measured with standard methods. Harvested plant parts and soil samples were digested and analyzed for copper, zinc, lead, cadmium and chromium contents using Atomic Absorption Spectrophotometer. The transfer factor and bioconcentration factor of the test plants were determined with standard models. Data were subjected to Analysis of Variance while Duncan's Multiple Range Test at $p \leq 0.05$ was used to separate the means.

The findings of the study were that:

- (i) rice biochar had pH (8.54), ash (52.37%), Mg (0.70%), K (11.88%) and Si (14.36%) contents while sorghum biochar had pH (8.41), ash (35.07%), Mg (0.69%), K (7.89%) and Si (14.72%) contents;
- (ii) the biochars possessed micropores and macropores and functional groups such as OH (3400 cm^{-1}) and aromatic compounds, C-H ($900\text{ to }885\text{ cm}^{-1}$);
- (iii) biochars significantly ($p\leq 0.05$) increased soil properties such as pH (20.66%), water holding capacity (36.67%) and porosity (37.29%) but significantly ($p\leq 0.05$) reduced heavy metals below the permissible limits recommended by WHO;
- (iv) rice biochar at 3% increased the height of the plants: *Pennisetum glaucum* (76.03%), *Zea mays* (81.50%), *Tithonia diversifolia* (39.27%) and *Tridax procumbens* (66.42%) while sorghum biochar at 3% increased the height of the plants: *Pennisetum glaucum* (157.61%), *Zea mays* (23.01%), *Tithonia diversifolia* (83.33%) and *Tridax procumbens* (66.66%);
- (v) the biochars significantly reduced ($p\leq 0.05$) the availability of Cu, Zn, Pb, Cd and Cr; and
- (vi) only *Zea mays* extracted Cu and Cr while others stabilised the HMs.

The study concluded that RSSB amended spent oil-contaminated soil by reducing the availability of the HMs and improving the properties and nutrients required to support plant growth. The study therefore recommended the two biochars for the remediation of SOS.

CHAPTER ONE

INTRODUCTION

Spent oil is any refined oil from natural or fabricated oil which was used and contaminated by physical or chemical impurities resulting from its use (USEPA, 2000; MEF, 2008). Tyson-Young (2008) defined spent oil as petroleum or synthetic oil from industrial and non-industrial sources, obtained for lubricating uses which has made it to become unsuitable for its initial use because of the impurities present in the spent oil. The chemical name for spent oil is used mineral crankcase oil (DOE, 1989) which is yellowish brown to black in colour and insoluble in water at 20°C. Spent oil is an heterogenous mixture that constitute a very large amount of chemicals with unfamiliar biologic activity involved that which is genotoxic (Clonfero *et al.*, 1996). The toxicity of waste engine oils has been assigned to its chemical composition which varies widely depending on the original crude oil, the refining processes, types of additives and the efficiency of the engine (Obinia and Afiukwaa, 2013).

Spent oil contains metals like iron, steel, copper, lead, zinc, barium, manganese, arsenic, cadmium; additives like detergents, metallic salts such as molybdenum and zinc salts; sulfur, water, ash and polycyclic aromatic hydrocabons (PAHs) (ATSDR, 1997). Majority of heavy metals like aluminium, lead, iron and nickel below detection in unused oil were found to be very high in used oil making them to be harmful to the environment (Davis *et al.*, 2001; Abioye *et al.*, 2012). These heavy metals are regarded as pollutants to the environment (Dickson and Udoessien, 2012; Fatoba *et al.*, 2015). These metals could be stored as base metals, hydrated oxides, carbonates, exchangeable positively charged ions in soils or they attached with biological components of the soil (Stengel and Gelin, 2004).

The nature of heavy metals resulting from their inability to break down makes them toxic to the environment especially when they are beyond the permissible limit (Xu *et al.*, 2014). The continuous presence of these contaminants is becoming a threat to human safety as well as the environment (Paz-Ferreiro *et al.*, 2014). The translocation factor of a certain metal to plants is influenced by the kind of plant, for example, cadmium is mainly regarded as a toxic metal in soil as a result of its high transfer factor for any plant (Javied *et al.*, 2009; Khan *et al.*, 2010). Metals like copper and cadmium are present in polluted soils. Heavy metals mobility can be disturbed by oxidoreduction and acid-base properties of metal ions (Uchimiya *et al.*, 2010). Zinc and lead remain in soil, whereas chromium, copper, and cadmium pass through soil pore water (Uchimiya *et al.*, 2010). A complex compound result from the reaction of Cadmium and Cu with available soil organic matter (Uchimiya *et al.*, 2010). The sources in respect to Cu are liquid waste, municipal composts, mining wastes, and copper-containing antifungal agents (Uchimiya *et al.*, 2011a). Higher level of Cu results to the reduction of microflora and fauna population in the soil (Mackie *et al.*, 2015) and also leads to gastrointestinal cancer when Cu polluted crop is being consumed (Turkdogan *et al.*, 2003).

The significant human-induced sources of Cd in the ecosystem are incineration, smelting, nickel-cadmium batteries (WHO, 2010). There has been increased Cd level in polluted soils which resulted from frequent fertilizers application and sewage sludge on arable soils (Lu *et al.*, 2015). The sources of Zn production include smelting, production of cosmetics, metal coating, television, rubber and tire industries (Baccio *et al.*, 2005). Zinc is less toxic as compared to other metals but toxic at higher concentrations (Baccio *et al.*, 2005). Organic material, pH and type of parent material influence the Zn presence in soil (Alloway, 2009; Ivezic *et al.*, 2012; Perez-Esteban *et al.*, 2013). Zinc, a transition element and an essential micronutrient is the most

frequently existing trace heavy metal in agro-ecosystem (Baccio *et al.*, 2005). Weathering and oxidation processes are the causes of Pb increase in soil after which it is adsorbed on the soil particles and are accumulated in plants and animal bodies (Ahmad *et al.*, 2012).

From Boughton and Horvath (2004) research, an estimate of 45% of used oil were obtained globally while the 55% is disposed into the environment by the final user. In Nigeria, Opeyemi (2004) revealed that roughly 300 million litres of engine oil went into sales annually together with estimate of roughly 150 million litres of spent oil generated annually. Bamiro and Osibanjo (2004) reported an estimate of over 200 million litres of spent oil generated per annum in 2004. About 75% of this figure came from spent engine oil while industry based used oil covers the remaining 25 % (Obinia and Afiukwaa, 2013). In some parts of Imo State, Udebuani *et al.* (2011) reported that estimate of 4710 litres weekly of spent oil were released into the environment.

Spent oil poses a serious threat to the environment as a result of higher production of mineral crankcase oil, improper disposal and lack of policy for recycling after use (Bamiro and Osibanjo, 2004; El-Fadel and Khoury, 2004). In some emergent countries, there is no appropriate management of this used oil (Sempebwa and Carpenter, 2009). El-Fadel and Khoury (2004) suggested that spent oil can be refined to new engine oil and also can be re-used. The disposal of spent oil into the environment needs to be alienated for the sake of human safety and protection of the environment (Opeyemi, 2004). Some countries have laid down rules and regulations to control the release of their spent-oil for the protection of the environment. In most developed countries, spent oil is being recycled. It can be used directly as fuel, re-refined to fuel oil and regenerated to base oil (Kristensen, 2006).

Oil pollution renders soils infertile for decades, reducing plant growth and development (Dale *et al.*, 2006). Land has been degraded as a result of oil spilling, deliberate release of engine oil, use of chemicals and unwanted substances from vehicle and industries, thus having negative impact on the ecosystem. Oil pollution was revealed to be the main cause of environmental pollution in some areas that produce oil in Nigeria (Shell Nigeria, 2014). In Nigeria, there was a report that over 87 million litres of used oil were wasted yearly (Anon, 1985) and there was no concern about this disposal of oil (Anoliefo and Vwioko, 1995). The ecosystem has been victimized by these oil producing areas with heavy metals.

Heavy metals like zinc, lead, nickel, chromium and cadmium have been revealed to be oil component (Dickson and Udoessien, 2012), and are regarded as heavy metals, causing pollution of the environment (Shtangeeva, 2006; Fatoba *et al.*, 2015). Other metals include cobalt, iron, arsenic and silver (Nagajyoti *et al.*, 2010). These pollutants are hazardous and not valued as a result of their negative effects on the environment and human safety (Guilbert, 2003; WHO, 2010). The increased contents of these pollutants through spilling of oil impose harmful substance on soil which could lead to absorption by plants giving rise to their bioaccumulation in plants and finally causing toxicity to the food chain (Ekundayo and Obuekwe, 2000).

Plants are continuously introduced to unfavourable environmental conditions that are not beneficial to their lifecycle and yield by altering their physiological and metabolic processes (Kalaivanan and Ganeshamurthy, 2016). Ogboghodo *et al.* (2001) noted that land degradation as a result of oil pollution could lead to alteration of soil structure, compactibility and permeability. Moreover, chemical properties could be affected (Odu, 1981). Nwankwo (1989) reported that spent oil inhibits seed germination in plants. Oil penetrates and accumulates in plant thereby damaging the membranes and causing discharge of cell contents (Baker, 1970). Oil contaminated

soil has negative effect on cereals by causing yellowing of leaves and water loss (Udo and Fayemi, 1975). Contaminated plots had significantly lower total vegetation cover and litter than uncontaminated plots (Diana *et al.*, 2004).

Sustainability comes into place when valuable resources are losing their qualities. Environmental sustainability is a reasonable interaction with the environment to avoid depletion or degradation of natural resources so as to sustain the existing and later generations (John, 2011). This can be possible by managing and securing the natural resources for our needs today and for future. In natural environment, without human interference, the environment has an interesting way of protecting itself. For instance, when a tree falls, decomposition takes place which result to availability of nutrients to the soil. These nutrients nourish the soil creating suitable conditions for the future saplings to survive. Environmental sustainability would be in place if humans can take actions to reduce the use of physical resources, recycle whatever resource that has been used, use renewable resources rather than depletable resources, create strategic methods of eliminating production of toxic materials and protect as well as bring to life the natural habitats (Sutton, 2004).

Soil as one of the natural resources has been threatened by contaminants released on it, therefore, its sustainability is needed. Soil degradation resulting from anthropogenic activities has become urgent concern (Jien *et al.*, 2015). Soil can be rescued through sustainable agriculture (Kamara *et al.*, 2015). This involves the use of farming techniques that will protect the environment such as less dependence on chemicals and introduction of soil amendments to improve the soil nutrient. These could reduce the mineral content of added organic matter and helps to sequester carbon in soils to facilitate soil sustainability (Bolan *et al.*, 2012; Troy *et al.*, 2013). Amendment agent for soil such as biochar could be encouraged in this context. The key features of biochar that makes

it exceptional as an amendment agent for soil is its high porosity nature and surface area potentially responsible for improved water retention and its high sorption capacity respectively (Glaser *et al.*, 2002; Warnock *et al.*, 2007; Sohi *et al.*, 2009).

It is understood that biological and chemical stability contribute to biochar's ability to pose as a carbon sink which is beneficial to soil that are long-lived (Sohi *et al.*, 2009). Introduction of organic content like fertilizers and dungs has been used to retain nutrients in soil and remain available to crops but biochar is much more effective and a stable nutrient source (Chan *et al.*, 2007; Zheng *et al.*, 2010). Biochar plays a key role in phytoremediation of soil (Rizwan *et al.*, 2016). Oxygenated functional groups, increased pores, high surface area and increased cation exchange capacity of biochar are key features that help in the immobilization of pollutants (Gaskin *et al.*, 2008; Beesley *et al.*, 2010; Lee *et al.*, 2010; Mukherjee *et al.*, 2011; Harvey *et al.*, 2012; Ahmad *et al.*, 2014).

Biochar is a minute and poriferous substance which is similar to charcoal in appearance generated by the combustion of green wastes and livestock wastes in the absence or limited oxygen for environmental sustainability (Hans-Peter, 2013). The International Biochar Initiative (IBI) defined biochar as a substance made through charring of feedstocks (IBI, 2015). It is an environmental black carbonic sorbent in soils (Knicker *et al.*, 2005). It is a substance that has been produced under conditions modified to achieve distinguishing features which include high surface area to volume unit and little quantity of residual resins, having a useful function for agriculture and the environment, (Lehmann and Rondon, 2006). Char, activated charcoal, charcoal and other black charcoal substances are other types of char which are produced industrially though the differences are relatively elusive since they are gotten from heating of carbon rich biomass.

Natural occurrence such as forest and grassland fires brought biochar into existence which is continued in soil matrix (Skjemstad *et al.*, 2002; Sohi *et al.*, 2009). Between 450 BC and 950 AD, Amazonian dark earth and brown earth soils in the Amazon Basin were formed due to the indigenous practice (Barrow, 2012). They were found to be highly rich and fertile as compared to relatively infertile soil surrounding it (Glaser, 2007; O'Neill *et al.*, 2009; Almuth, 2011). Gradual process of accumulation of black carbon present in the soil contributes to the soil fertility and the richness of carbon (Solomon *et al.*, 2007). Evidence showed that concentrated mass of biochar in soil is possibly useful under certain circumstances that arise from *terra preta* and *terra mulata* (Glaser, 2007; Pagano *et al.*, 2016). An instance reported by Ponomarenko and Anderson (2001) showed the fertile black earth, existing across Western Canada, have 25-65% carbon formed from black coal. Half-life dating also proved that woodland soils in East-Central British Columbia consist of carbon made out of biochar which ranged from 182 to 9558 lifespan (Sanborn *et al.*, 2006).

Thermal degradation of cellulose at relatively high temperature results in reasonable weight reduction that exists as volatiles, remaining a rigid uncrystalized charcoal (Lehmann and Joseph, 2015). In pyrolysis, aromatic carbon in the biochar increases with increase in temperature (Lehmann, 2007). As a result of increase in volatile matter reduction (other products released are water, followed by hydrocarbons, tars, vapours, H₂, CO and CO₂) leading to alkyl and O-alkyl C being converted to aryl C (Baldock and Smernik, 2002; Demirbas, 2004). Carbonization occurs at higher temperature (>600°C) leading to the removal of non-C atoms thereby increasing carbon content which may be up to 90% (in woody biomass) but could be less than 70% in straw derived biochar (Antal and Gronli, 2003; Demirbas, 2004).

Biochar is composed of heterogeneous substances which are stable and labile (Sohi *et al.*, 2009). Antal and Gronli (2003) regarded fixed carbon, volatile VM, water and ash contents as its major components. The biochar constituents determine its physical, chemical and functional behaviour (Brown, 2009), resulting to its adequacy for soil amendment in the environment (Downie *et al.*, 2009). Conforming to Sohi *et al.* (2009), production of biochar from different type of feedstocks under various carbonization does not alter the constancy of elevated carbon content and strong aromatic structure that makes it to be chemically stable.

Virtually natural resources can undergo pyrolysis, energy transformation capacity, the biochar quality and by-products (bio-oil and syngas) depends on type of the raw material. For energy loss reduction, the materials to be pyrolyzed must have low moisture content <10% by mass (Wu *et al.*, 2012). Biochar is produced through exposure of raw material to heat with limited or without oxygen (Lehmann, 2007). Sustainable biochar is made from sustainably secured feedstocks like plant and animal materials making use of contemporary pyrolysis technique (Woolf *et al.*, 2010). Traditional method of charcoal production causes pollution to the ecosystem by releasing the energy and pollutants into the ecosystem (Woolf *et al.*, 2010). In modern pyrolysis, energy produced from the combustion of biomass is captured in gaseous (syngas) or liquid (bio-oil) forms leaving behind char (biochar) as a by-product (Zheng *et al.*, 2010; Almuth, 2011; Gul *et al.*, 2015). Biochar pyrolysis emits more energy when compared to its consumption, this depends on the water content of the biomass (Lehmann, 2007). Presently, there are various thermo-chemical technologies which include pyrolysis and gasification for biochar production.

Pyrolysis is the burning of biomass without or with little oxygen to produce by-products: biochar, bio-oil, and syngas (Gul *et al.*, 2015). Pyrolysis is a simple and low-cost method used to

generate charcoal for millenia (Zheng *et al.*, 2010). It is the most common method for producing biochar (Almuth, 2011). The biomass type used and the production conditions determine the biochar efficacy as an amendment agent for soil (McClellan *et al.*, 2007; McLaughlin *et al.*, 2009). Pyrolysis is classified into two: slow and fast pyrolysis.

Slow pyrolysis is the exposure of feedstock to heat at a low temperature in the with or without little oxygen producing biochar and its by-products (syngas and bio-oil). (The liquid produced are in two phases: a pyrogyneous water and decanted oil. Kilns, retorts and converters are used for slow pyrolysis (Garcia-Perez *et al.*, 2010). Slow pyrolysis has the following advantages over other thermochemical conversion technologies:

- inexpensive;
- accomodates diverse sources of feedstock;
- reduction of feedstock to particle size is not necessary;
- long residence time of feedstock in the reaction chamber;
- high quantity of biochar and little quantity of usable energy products are produced;
- production of high-quality biochar biochar determined by the selected application, type of biomass and details of thermochemical process; and
- suitable for the supply of little amounts of heat (Brownsort, 2009; Pecha and Garcia-Perez, 2015).

Fast pyrolysis is a method whereby particle sized organic material is subjected to heat at a high temperature in a designed reactor (Garcia-Perez *et al.*, 2010) to yield 60-70% weight of the feedstock as bio-oil and 15-25% weight as biochar (Bridgwater *et al.*, 2001; Czernik and Brigwater, 2004; Mohan *et al.*, 2006). Feedstock undergoes heating from the temperature of 400-

700°C without oxygen. There must be a reduction in the feedstock particle size to < 2mm so as to get rapid heating rate which requires significant amounts of energy (Cummer and Brown, 2002). Bio-oil, being the main byproduct for the biomass is a dark brown liquid generated from the pyrolysis. The other pyrolysis method is gasification. Gasification is a thermo chemical process (600-1400°C) which involves heating of biomass with high temperature and a little amount of air in the reaction chamber to produce a main product-syngas (Zheng *et al.*, 2010; Almuth, 2011) with little biochar at most 10%. The gas majorly consists of CO, H₂, CO₂ and traces of CH₄ (Higman and Burgt 2008). Some of the water vapor generated is being converted to H₂ (Narzari *et al.*, 2015).

Intensive agricultural practice and poor management scheme without adequate recuperative measures to revive the soil have led to decline in soil fertility and biodiversity (Ndor *et al.*, 2015). The particular temperature of natural feedstock for biochar production promotes its ability of persistency in soils with minor decomposition in creating friendly habitat for microorganism survival (Lehmann and Rondon, 2006). Efficiency of biochar as an amendment agent for soil is a method that is related to the conventional “slash-and-burn” practice, which involves the removal of vegetation and introduction of nutrients in the soil for fertility purpose. However, this practice has not been favourable to the environment because of deforestation and air pollution (Zheng *et al.*, 2010). Biochar could stay in soil over centuries as a result of its resistant ability to microbial activities related to decomposition. This feature could be affected by the conditions that surrounds the production and the kind of feedstock used during pyrolysis (Zheng *et al.*, 2010).

Biochar can be introduced progressively and mixed with fertilizers which improves the soil quality thereby increasing crop production (Ndor *et al.*, 2015;). Biochar as an amendment agent

of soil possess the capacity to enhance soil quality as well as change the physico- chemical properties of soil having the intention to boost agricultural yield (Lehmann *et al.*, 2006; Lehmann, 2007; Jeffery *et al.*, 2011; Liu *et al.*, 2013; Paz-Ferreiro and Fu, 2014; Colantoni *et al.*, 2016). The quality of soil can be achieved through biochar by soil pH increase, high moisture holding capacity, providing convenient habitat for the microorganisms, increasing CEC, and improving the retention of nutrients (Curaqueo *et al.*, 2014; Gul *et al.*, 2015). Biochars made from manure and bone meal-derived feedstocks contain high nutrient content and boosts plant growth (Amonette and Joseph, 2009; Uzoma *et al.*, 2011; Hass *et al.*, 2012; Lentz and Ippolito 2012). Biochar as a soil conditioner could possibly possess combined advantage which may potentially enhance activity of microbes and decrease nutrient losses (Dias *et al.*, 2010).

Decay of organic materials results to discharge of greenhouses gases into the atmosphere (Liang *et al.*, 2008). Pyrolysis of these organic materials retains much carbon to become well stable in nature. Application of the derived biochar to soils helps in effective carbon sequestration (Liang *et al.*, 2008). Approximately, this method can be used to “fix” carbon for the reduction of ongoing global carbon discharge to a feasible extent of 10 percent (Woolf *et al.*, 2010). Biochar possess the capacity to capture carbon from the airspace and convey into soil (Winsley, 2007; Gaunt and Lehmann, 2008; Laird, 2008; Ndor *et al.*, 2015). Biochar with high temperature possibly reduces greenhouse gas emissions as a result of high recalcitrant carbon (Gascó *et al.*, 2012; Brassard *et al.*, 2017; Xiao *et al.*, 2018).

A widespread pollution of soil with organic and inorganic pollutants has remained a threat to the ecosystem (Adams *et al.*, 2007). Reports varied on the different heavy metal remediation which could be as a result of the biomass type and pyrolysis of biochar. It is mandatory to weigh up the key properties of biochar responsible for heavy metal remediation during selection of biochar

(Lima *et al.*, 2014). Biochar aromaticity can be improved by the increase in temperature used for the purpose of biochar production (Harvey *et al.*, 2012; McBeath *et al.*, 2013). Biochar is able to remediate polluted soil by decreasing the rate at which heavy metals are being take up (Semple *et al.*, 2004; Yang *et al.*, 2016; Trakal *et al.*, 2018) thereby resulting in reduced metal uptake by biological organisms and probably reducing the toxic effects (Gomez-Eyles *et al.*, 2011; Park *et al.*, 2011; Oleszczuk *et al.*, 2012). Biochar alkaline nature could help metals to precipitate from solution to the surface of biochar thereby lowering the available contaminants to plants (Zhang *et al.*, 2013; Inyang *et al.*, 2016).

1.1. Statement of problem

Sustainable agriculture is a method of producing healthy food for the public by creating no harm to the ecological community (Zheng *et al.*, 2010). Sustainable agriculture has been faced with two major problems of low nutrient in the soil and quickened mineralization of soil organic material (Renner, 2007). Contamination resulting from used lubricant is one of the environmental challenges in Nigeria contributing to these problems mentioned earlier and obviously more widespread than crude oil pollution (Edebiri and Nwanokwale, 1981; Odjegba and Sadiq, 2002; Lale *et al.*, 2014). Spent lubricant is carelessly discharged into the environment after repair of car and generator engines in garages, service stations and industrial sites (Lale *et al.*, 2014). In Nigeria, reports accounted for over 150 million litres of used oil discharged annually (Bamiro and Osibanjo, 2004).

The chemical compound in spent oil that are of health and environmental concerns include heavy metals, polycyclic aromatic hydrocarbons and chemical additives like amines, phenols, benzenes, metal oxides and trace metals (Smith *et al.*, 2006; Ogbeide, 2010). This has contributed

negatively to the physico-chemical and biological characteristics of soil, crop yield and safety of plant materials for consumption.

1.2. Justification of the study

Several reports warned about the negative effects of pollutants in the ecosystem, including plants. Impacts on arable soil include soil degradation and depletion of soil biodiversity (Foley *et al.*, 2005; Robertson and Swinton, 2005; Ndor *et al.*, 2015). Various soil remediation technologies such as physical and chemical techniques for example washing (Paria, 2008; Svab *et al.*, 2008), venting (Nobre and Nobre, 2004; Hoier *et al.*, 2007), thermal treatment etc (Araruna *et al.*, 2004) and bioremediation have been developed and ameliorated on the basis of soil standards for the protection of human health and ecosystem. However, most of these techniques are sophisticated and expensive. Though, bioremediation has been of relative importance in the remediation of pollutants. It is necessary to seek less sophisticated method of remediating the contaminated soils. Biochar could serve as a tool to address these limitations. It can effectively contribute to sustainable soil regulation by decreasing environmental impact of pollutants on soil and improving soil productivity.

Biochar technology is simple and readily available to the developing world. The key features of biochar that considers it as an amendment agent for soil is its highly porosity, increased surface area which contribute to the increase in water holding capacity and high sorption capacity (Warnock *et al.*, 2007). Lehmann and Rondon (2006) suggested biochar introduction as a feasible method to enhance seriously deteriorated soils. Adoption of biochar management promotes effective and eco-friendly use of existing resources (Lehman and Rondon, 2006). High volume of wastes is generated from agriculture in sub-Saharan Africa. They are prospective

biomass for generating biochar. The efficacy of biochar can at best be evaluated through the cultivation of plants in the biochar-amended soil. Moreover, there is the need to investigate the potential of plants in this respect, hence, the need for good candidates.

1.3. Aim of the study

This research study aimed at characterizing biochars produced from rice and sorghum straws and determining their effects on the mobility of heavy metals (cadmium, chromium, copper, lead and zinc) in selected plants (*Zea mays*, *Tithonia diversifolia*, *Pennisetum glaucum* and *Tridax procumbens*) grown in spent oil-contaminated soil.

1.4. Specific objectives

The specific objectives of the study were to determine the:

- (i) physicochemical and functional properties of locally produced sorghum and rice straw biochars;
- (ii) effect of biochars on the physicochemical properties of spent oil-contaminated soil;
- (iii) effect of biochars on the growth of selected plants grown in spent oil- contaminated soil;
- (iv) effect of different concentrations of biochars on the mobility of heavy metals (Zinc, Copper, Cadmium, Lead and Chromium) in selected plants grown in spent oil-contaminated soil; and
- (v) phytoremediation potentials of the selected plants.

CHAPTER TWO

LITERATURE REVIEW

2.1. Effect of oil on soil and plants

Deficiency of available forms of Nitrogen and Phosphorous could result from the negative effect of contaminated soil (Wyszkowska and Kucharski, 2004). These also have negative effects on its metabolic activity, physico-chemical properties of soil and plant production (Wyszkowski and Ziolkowska, 2008; Uchendu and Ogwo, 2014) depending on the level of the oil, nature of soil and other related factors (Agbogidi and Egbuchua, 2010). Ogboghodo *et al.* (2001) noted that oil contamination could alter the soil physico-chemical properties such as soil structure, soil permeability as well as compaction. Infiltration rate, moisture content and soil porosity (Agbogidi and Enujeke, 2012; Nwite *et al.*, 2012; Nwite and Alu, 2015), soil pH and nutrient mobilization (Dick, 2007) were also affected. Wyszkowski and Ziolkowska (2008) also revealed that polluted soil significantly reduced soil organic matter. Ahamefule *et al.* (2014) concluded that soil polluted with 1– 3 % used lubricating oil significantly decreased water retention capacity.

Diana *et al.* (2004) reported scanty vegetation cover on oil contaminated sites as compared to non-contaminated sites studied. Spent oil reduced the percentage seed germination as a result of the oil covering the seed surfaces which led to disturbance in the physiological activities in the seed (Udo and Fayemi, 1975; Amadi *et al.*, 1993). Agbogidi and Nweke (2005) and Agbogidi *et al.* (2006) indicated that significant decrease in the growth of Okra and five cultivars of Soy beans on spent oil polluted soil. Daniel-Kalio and Pepple (2006) demonstrated that plant height, leaf area and dry weight of *Comelina begalensis* were significantly higher at control level when

compared to 50 mg g⁻¹ treatment. Furthermore, Ibmesin (2010) indicated that vegetative cutting of sour grass thrived better in control and 75% of the studied plants survived in soil polluted at low concentration while the heavily polluted soil resulted to the death of the plants.

From studies, oil contaminated soil affected plants in the following ways; transfer of toxic substances in vegetative tissue (Baker, 1970), low biomass production (Brandt *et al.*, 2006; Adenipekun *et al.*, 2008). Udo and Fayemi (1975) reported retardation of growth and leaf chlorosis in plants grown in oil polluted soil. Adu *et al.* (2015) reported that soil contamination with used and unused engine oil could have negative influence on the vascular network of the *Vigna unguiculata* growing in such environment as a result of heavy metals available. Ahamefule *et al.* (2014) posited that the negative impact of oil on soil properties generally did not promote the growth of maize. Heavy metals are built up in oil contaminated soil resulting to metal transfer into plant tissues (Vwioko *et al.*, 2006). Moreover, Ubuoh *et al.* (2016) confirmed that there was adverse impact of oil on the growth together with biomass yield of *Panicum maximum*. Nwite and Alu (2015) also confirmed negative effect of spent oil on maize.

2.2. Sorption mechanism of biochar

Sorption is a situation whereby a substance gets bonded to another. The following terminologies are associated with sorption of which biochar possess in reducing heavy metal availability.

- Absorption - the immersion of gas or liquid into liquid or solid substance respectively. The absorbent which can be either liquid or solid receives the absorbate that is either gas or liquid and expands in size and volume as a result of the absorption that occurred.
- Adsorption – this is a process whereby gas or liquid is being collected in ions and molecules on the surface of another substance of different state (adsorbent) (e.g. reagents

adsorbed to a solid catalyst surface). In this case, the adsorbent still maintains the size of the outer part while the internal part is being altered by receiving the adsorbate to fill up the pores present in it.

- Ion exchange: this is a sorption phenomenon whereby ions in liquid form moved into a solid matrix after which ions of a different type but of the same polarity are being let out.

Demonstration of surface sorption of heavy metals on biochar has been made with the use of Scanning Electron Microscopy (SEM) (Beesley and Marmiroli, 2011; Lu *et al.*, 2012). The key features responsible for biochar quality includes increased adsorption rate, cation exchange capacities and low levels of mobile matter (tars, resins, etc) (Glaser *et al.*, 2002; Liang *et al.*, 2006; McClellan *et al.*, 2007; McLaughlin *et al.*, 2009). Sorption capacity increases in biochar when compared to organic fertilizer as a result of increased surface area, negative surface charge and charge density ((Liang *et al.*, 2006) and resistant to degradation (Sizmur *et al.*, 2015). Application of biochars have been investigated both in laboratory and field scales as *in situ* remediation strategy for both organic and inorganic contaminants by boosting sorption capacity of soils and sediments (Cornelissen *et al.*, 2005; Cho *et al.*, 2009). Fellet *et al.* (2011) showed that the biochar applied to the mine tailings of Cave del Predil resulted to beneficial effects on bioavailability and leachability decrease of some of the contaminants which describe potential biochar as an amendment material for polluted sites.

Heavy metal movement is being reduced by biochar as a result of the alteration in their redox states (Choppala *et al.*, 2012). Biochar pyrolyzed at low temperature carries more of oxygen containing functional groups which create surface complex between cationic metals and biochar site (Beesley and Marmiroli, 2011; Uchimiya *et al.*, 2011a). A negatively charged biochar attracts the hydrogen ions from the soil, thereby increasing the soil pH (Sizmur *et al.*, 2015).

Particularly in acidic soil, reduced cation exchange capacity and total organic carbon soils, increase pH contributes to the metal sorption as a result of removal of proton from pH depending on the cation exchange surfaces on the soil (Uchimiya *et al.*, 2011a; Rees *et al.*, 2014). The functional groups of biochar affect the sorption process which is determined by the type of their surface charge with the aim of sorbing the metals onto the biochar surface (Amonette and Joseph, 2009). Mendez *et al.* (2012) noted that there was a connection between Cu^{2+} sorption and increased oxygen-containing functional groups, increased pore diameter, high superficial charge density and cation exchange content of biochar.

Biochar can effectively take out several positively charged metal ions and also take up negatively charged nutrients e.g phosphate ions (Lehmann, 2007). Carboxylic, phenolic and other oxygen-containing surface functional groups are formed as a result of slow and measurable *in situ* oxidation process which biochars undergo in soils (Cheng *et al.*, 2006). These oxygenated surface groups of biochars contribute to the elevated cation exchange capacity of soil (Lee *et al.*, 2010). Zheng *et al.* (2010) reported that unmodified biochar derived from waste feedstock had the capacity to efficiently take up two triazine pesticides, and still restrict their movement through the soil matrix.

Heavy metals are not degradable, hence biochar is introduced to reduce their availability to plant by building metal ions on their surfaces, adsorb them thereby providing a lesser risk (Uchimiya *et al.*, 2010). Uchimiya *et al.* (2011a) reported that cation exchange capacity (CEC) of biochar enhanced Cu retention in sandy loam soil while its sorption mechanism helped to withhold Cu in a clay soil with alkaline nature. Uchimiya *et al.* (2011b) noted that sorption desorption mechanism brings about increase in the rate at which soil solution comes to equilibrium when biochar is

being added to contaminated soil however, could enhance the sorption capacity of any new pollutants introduced to the soil.

On a certain note, there are some determinants of soil that affect metal complexation and effects of biochar application to soil. Addition of biochar significantly reduced the Cd and Zn in pore water obtained in the course of 60-day field experiment (Beesley *et al.*, 2010) and in leachate in a column experiment (Beesley and Marmiroli, 2011). Reports showed a reduction in Zn contents in sludge after application of pecan-shell biochar on acidic arable soil (Novak *et al.*, 2009). Laird *et al.* (2010) had a similar report on decreased Zn concentration with increasing application rates of dried swine manure biochar (0 to 20 g/kg) in loamy soil. They further pointed out that introduction of biochar reduced the content of Cu, P, K, Mg and Ca. Fellet *et al.* (2011) presented reduction in bioavailable (Diethylenetriaminepentaacetic extractable) Cd, Pb and Zn contents after amendment of mine tailings with 0-10% biochar derived from orchard prune.

2.3. Biochar properties

Biochar properties are influenced by wide range of factors which include the kind of feedstock, the particle size of the feedstock and temperature and conditions of production. These different biochar features have made some feedstock more suitable than other for the remediation of different heavy metals. Thus, selection of biochar as amendment agent for soil remediation depends on biochar properties like pH, surface area, ash and carbon contents of biochars. All these improve efficiency of biochar to restrict the heavy metals movement (Lima *et al.*, 2014).

Several reports have proved that biochar properties particularly enhance the plant growth and yield after being applied to soil (Cheng *et al.*, 2006, 2008; Major *et al.*, 2010). These studies were carried out in the tropics applying locally produced biochar to soils that are low in organic

matter content (Laird *et al.*, 2009). Occasionally, it was shown that biochar has negative or no impact on the soil when introduced to soil matrix (Laird *et al.*, 2009). The differences in the biochar result on plant growth depends on factors like biochar quality, application rates, type of soil and crop (Rawat *et al.*, 2019). Alkaline nature of biochar may have slight influence on the low contents of available metals in soils amended with biochar. Addition of biochar enhance the heavy metal precipitation in soils due to the increased pH possessed by biochar. The elevated pH value of biochar is influenced by the production temperature (Wu *et al.*, 2012), thus connected with high ash content (Cantrell *et al.*, 2012). Houben *et al.* (2013) postulated that pH could be responsible for the varying mechanism to heavy metal remediation in soil by different biochars.

The key feature of biochar is possession of large surface areas, that indicates ability for complexation of heavy metals on their sites. Metal sorption on biochar was carried out on several cases with the use of Scanning Electron Microscopy (SEM) (Beesley and Marmiroli, 2011; Lu *et al.*, 2012). This sorption could result from complexation of the heavy metals with different functional groups existing in the biochar, as a result of the interchange of heavy metals with cations related with biochar, such as Ca^{2+} and Mg^{2+} (Lu *et al.*, 2012), K^{+} , and Na^{+} (Uchimiya *et al.*, 2011c). Beesley and Marmiroli (2011) found out that biochar were able to take up and retain Cd and Zn on their surfaces. Beesley and Marmiroli (2011) noted that metal sorption occurred on the biochar surface and there was no immediate reversible process. Cadmium and Zn contents on the surface-water decreased 300- and 45-fold, respectively.

The ash content in feedstock determines the ash content found in biochar. Green and animal feedstocks generate biochar rich in ash contents in comparison to woody materials (Demirbas, 2004). Park *et al.* (2011) revealed that biochar made out of chicken droppings successfully reduced the extractable Cd and Pb contents except Cu while biochar derived from the plant

residue was better in reducing all the metals in a heavy-metal-contaminated soil and soil with natural pollution. Application of biochar elevated heavy metal that were attached to organic matter. Both biochars also reduced cadmium and lead in pore water of soil. The two biochars showed sorption capacity for Pb, perhaps owing to precipitation and complexation of Pb with carbonate, sulphate and phosphate that are available in these biochars. Karami *et al.* (2011) opined that phosphorus had a positive effect on Pb that was retained in polluted mine soil amended with biochar (psuedo-total lead; 2%). Regarding to the previous work, biochar application decreased Pb content from 80 mg to less than 40mg in porewater.

Uchimiya *et al.* (2012) demonstrated the effect of 10 biochars derived from 5 different biomass at 2 different pyrolysis temperatures. They noted that droppings with high or low portion of ash contents or phosphorus did not effectively restrict heavy metal movements. On the contrary, biochars pyrolysed at 700°C effectively stabilized the heavy metals, which may be due to feedstock modification which include the nitrogen containing heteroaromatic and leachable aliphatic functional groups which have been removed during pyrolysis. They observed stabilization of Cu and Pb contents in soil, while Cd and Ni responded positively to the biochar type applied to the soil.

Uchimiya *et al.* (2011b) carried out a study using biochars derived from woody feedstock and grass pyrolysed at the varied temperatures (650°C to 800°C) for heavy metal immobilization. However, Uchimiya *et al.*, (2012) carried out experiment using poultry droppings pyrolysed at four different temperatures to retain Pb. They reported that biochar pyrolysed at low temperatures were more effective than the ones pyrolysed at higher temperature as a result of the stabilizing capacity they possess. It is required for biochar derived from chicken litters to pass through high pyrolysis temperature to achieve same remediating capacity as plant-derived

biochars. Cao *et al.* (2009) showed that biochar pyrolysed at 200°C had a stronger effect in Pb sorption than biochar pyrolysed at 350°C.

2.4. Effect of biochar on soil properties and plant biomass

Biochar as an amendment agent for soil boosts crop growth and yield by enhancing the physico-chemical and biological properties of the soil (Glaser *et al.*, 2002; Lehmann *et al.*, 2003; Shaaban *et al.*, 2018). Collison *et al.* (2009) noted considerable moisture content up to 10% in biochar. Changes in porosity and size aggregation distribution The porous nature and distribution of size aggregation of biochar improves soil physico-chemical properties which include, porosity, pH and water holding capacity (De Pasquale *et al.*, 2012; Ouyang *et al.*, 2013) which contribute to the consistency of soils for crops. Studies reported increase in Ca and Mg in soil (Lehmann *et al.*, 2003; Major *et al.*, 2010; DeLuca *et al.*, 2015), increase in soil N and P (Glaser *et al.*, 2002; Lehmann *et al.*, 2006; Borchard *et al.*, 2012) and even ammonia emission capture as a means of returning available soil N (Taghizadeh-Toosi *et al.*, 2012), adsorption of pollutants from soil leachates (Beesley *et al.*, 2010; Beesley and Marmiroli, 2011; Fellet *et al.*, 2011) due to introduction of biochar to soil.

Various greenhouse and field experiments were performed to investigate the effects of biochars on plant growth (Glaser *et al.*, 2002; Yamato *et al.*, 2006; Chan *et al.*, 2007; Chan *et al.*, 2008). Majority of the works revealed that biochar application improved the plant yields. For instance, a field test where biochar derived from plant residue was used to amend soil, showed a positive effect of biochar on the soil properties and plant growth (Chan *et al.*, 2007). Field tests further revealed significant increase in plant yield resulting from the biochar addition (Glaser *et al.*, 2002; Yamato *et al.*, 2006). Studies indicated that both nitrogen fixation and mycorrhizal

activities in beans (*Phaseolus vulgaris*) are improved as a result of biochar addition (Rondon *et al.*, 2007; Warnock *et al.*, 2007). The appropriate proportion of biochar is dependent on the soil and crop type. Some studies indicated that much less proportion had better results (Glaser *et al.*, 2002).

Namgay *et al.* (2010) indicated that cadmium, arsenic and lead contents in corn aerial part reduced after addition of biochar. Beesley *et al.* (2013) also revealed that arsenic was elevated in soil pore water after biochar application. However, arsenic movement to the plants was decreased. This suggested that some biochars did not improve the heavy metals increase in crops. Therefore, the crops are secured for consumption. For the studies carried out in the humid tropics, Steiner *et al.* (2007) reported that plant growth increased with increasing biochar application rate up to 140 mgcha⁻¹ on weathered soils. Rondon *et al.* (2007) observed that biomass growth of beans (*Phaseolus vulgaris* L.) was elevated after biochar additions up to 60 mgcha⁻¹ however, dropped down to the same value of control plots after biochar addition was elevated to 90 mgcha⁻¹ (however, there was increase in the yield of beans). Steiner *et al.* (2007) also concluded that “biochar addition up to 50 mgcha⁻¹ had a positive effect on the crops and this has the tendency to reduce the plant growth at very high applications rate.”

Presently, field studies are initiated at different localities across the USA with use of biochars derived from different feedstocks (Almuth, 2011). Further investigations on interactions between various biochars, agricultural soils, climates and crops should be done (Dominic, 2008; Almuth, 2011). Fellet *et al.* (2011) suggested further studies on biochar application to polluted environments to decrease some bioavailable heavy metals in the soil. It can be envisaged from the results of previous work that described short term boosting of labile nutrients but large leaching losses after a relatively short time associated with amendments such as composts and manure,

that biochar could provide a mechanism of regulation in its combination with such amendments. Therefore, biochar application to soil provides a possible environmental advantage.

2.5. Plants and heavy metals

Pollution of arable soil by heavy metals has been a serious environmental problem as a result of their adverse effects on the ecosystem. Plants responds quickly to both lack and excess metal ions. Metal ions at higher concentrations such as cadmium and chromium are strongly harmful to the plants metabolism (Foy *et al.*, 1978). These harmful metals are regarded as soil pollutants as a result of wide range of phenomenon and their severe and persistent negative effects on plants from the affected soils (Reeves and Baker, 2000). Report was made on the alteration in catalytic capacity of enzymes in *Phaseolus vulgaris* and pea plants caused by high concentration of Cd and Zn (Somasekharaiah *et al.*, 1992; Romero-Puertas *et al.*, 2004). Toxic level of zinc caused unfavourable effects on root and shoot growth, chlorosis in the young leaves which could affect the older leaves as a result of prolonged exposure to excess Zn in plants (Ebbs and Kochian, 1997; Fontes and Cox, 1998).

High levels of Cd found in plants grown in contaminated soil showed visible symptoms like yellowing of leaf, leaf rolls, growth retardation, brown colour on the root tips, and eventually mortality (Mohanpuria *et al.*, 2007; Guo *et al.*, 2008). Generally, cadmium was found to restrain the intake and movement of some elements, such as Ca, Mg, P, and K and water in plants (Das *et al.*, 1997). Hattab *et al.* (2009) discovered alteration in physiological effects and photosynthesis of pea (*Pisum sativum* L.) due to excess Cd and Cu concentration. Copper is known to be a microelement for plants (Thomas *et al.*, 1998) and functions in carbon fixation and ATP synthesis. Cu constitutes various proteins such as plastocyanin in photosynthesis (Demirevska-

Kepova *et al.*, 2004). Excess copper in soil causes a toxic effect to plant cells, causes stress and injury to plants resulting to hindrance in growth of plant and yellowing of leaves (Lewis *et al.*, 2001).

Chromium affects activities in photosynthesis such carbon fixation, electron transfer, photophosphorylation, and enzyme activities (Nagajyoti *et al.*, 2010). Chromium stress induces metabolic activities in plants such as pigments reduction (Boonyapookana *et al.*, 2002). Chromium affects the higher plants at 100 µg/kg dry weight as a result of its toxicity (Davies *et al.*, 2002) and seed germination is the first to be influenced. In this respect, germination can be improved by the level at which plant tolerate Cr in soil thereby making the plant an indicator (Peralta *et al.*, 2001). Seed germination of *Echinochloa colona* decreased to 25% with 200 µM Cr and similarly in beans (Parr and Taylor, 1982; Rout *et al.*, 2000). Peralta *et al.* (2001) showed that 40 ppm of Cr (VI) decreased by 23% germination rate of Lucerne seeds (*Medicago sativa* cv. Malone) grown in the contaminated medium. It was observed in sugarcane that germination decreased by 32% and 57% with 20 and 80 ppm Cr, respectively (Jain *et al.* 2000).

Lead gets easily transported and accumulated in various plant parts. It has negative influence on morphology, growth and physiological activities in plants. Increased lead content in plant give rise to symptoms such as growth retardation, yellowing of leaves and darkening of roots (Sharma and Dubey, 2005; Nas and Ali, 2018). Reactions of lead with sulfhydryl groups result to inhibition of enzymatic activity at cellular level (Nagajyoti *et al.* 2010). Excess Ni²⁺ in soil has chronic effect on different physiological activities and causes various toxic effects like yellowing of leaves and plant death in various species (Pandey and Sharma 2002; Rahman *et al.* 2005; Yadav, 2010). The reduction in water intake showed the level of Ni chronic effects in plants (Pandey and Sharma, 2002; Gajewska *et al.* 2006). Studies on responses of *Tithonia diversifolia*

on contaminated sites can act as indicators for soil improvement which is responsible for a cheap sustainable strategy of cleaning up the environment (Obilo and Ogunyemi, 2005). Plants possess different mechanisms in the regulation of concentrations of metal ions and reduction of being exposed to heavy metals. Tolerance of plant to a specific metal is based on the interrelationship of physiological and molecular mechanisms. There is need to understand these mechanisms in developing plants as phytoremediators. Plants resist surplus heavy metals through adaptation (Meharg and Hartley-Whitaker, 2002). In the first stage of defense, most plants prevent or reduce uptake into root tissues when exposed to toxic metal include: restriction of metal ions to the apoplast, binding them to the cellular exudates and inhibition of further transport (Manara, 2012). If these methods did not work, existing metals in the cell are approached by the use of storage and detoxication methods, movement restriction and synthesis of certain heavy metal transferers, chelated compounds, and heavy metals capture by particular ligands e.g phytochelatins (Kalaivanan and Ganeshamurthy, 2016).

Phytochelatins are sulphur rich peptides that act as major components of Cd- binding complexes in many plants. It detoxifies Cd and bind it with other heavy metal like Cu, Zn or As through the thiol and carboxylase (Cobbett and Goldsbrough, 2002; Mudgal *et al.*, 2010). After the options have been used up, activation of defense mechanisms such as oxidative stress occurred opposing the results of reactive oxygen species (ROS) and Methylglyoxal (MG) such as regulation of antioxidant and glyoxalase system, and the plants synthesize stress-related (hormones, the biosynthesis of polyamines and proteins) and signaling molecules, such as salicylic acid and nitric oxide (Hossain *et al.*, 2011).

Reports have been carried out and confirmed that a medicinal plant act as a Cd hyperaccumulator (Marquard and Schneider, 1998; Masarovičová *et al.*, 1999; Král'ová *et al.*, 2000). Masarovičová

and Kráľová (2007) classified *Hypericum perforatum* as Cd hyperaccumulator due to high content of Cd in the shoot dry mass. Chelated compounds react with specialised metabolites of *H. perforatum* to improve its ability to tolerate metals. Similarly, Masarovičová *et al.* (2011) reported chelation of Cd ions with hypericin in *H. perforatum*. Chromium toxicity to plants is determined by its valency such as Cr(VI) which has chronic effect and motile and Cr (III) is less chronic (Lionel and Karunakaran, 2017). Chromium causes harmful effects on the physiological activities of plant. Exposure of plant to Cr alters plant metabolism by directly affecting the enzymatic activities or other metabolites or capacity to produce ROS that may result to oxidative stress (Shanker *et al.*, 2005). It was further pointed out that plants producing specialised metabolites (medicinal plants) could create adaptive methods of tolerance. This method is interrelated with chelation of metal ions by some certain specialized metabolites such as hypericin and pseudohypericin found in *H. perforatum*. Conversion of the chronic ionic type of metal into non-chronic metal ions occurred. The peri-hydroxyl groups located in the neighbourhood of the carbonyl groups show the best prerequisites to produce chelates with transition metal ions. However, Palivan *et al.* (2001) reported that reaction of copper complexes with hypericin in solutions with the use of Electron Paramagnetic Resonance (EPR) spectroscopy and discovered that hypericin produces a four-coordinated copper species where the solvent involved in the relationship of the metal.

As a result of the above interaction, free metal ions reduces thereby diminished their chronic effect. It was concluded that medicinal plants possessing specific secondary metabolites are able to form complexes with heavy metal for their tolerance against divalent metal (Lomaglio *et al.*, 2016). It was also confirmed that *Matricaria recutita* species grown in contaminated soils tolerate high Cd concentrations in shoots (Grejtovský and Prič, 2000; Masarovičová *et al.*, 2003).

It was pointed out that *M. recutita* which is one of the most favoured medicinal plants all around the world (Masarovičová and Král'ová, 2007) was regarded as Cd hyperaccumulators. The plant has a different labile specialised metabolites such as chamomillol, gossonorol, cubenol and herniarin (Masarovičová and Král'ová, 2012) to mention but few. It was confirmed that chamomile plants (*Matricaria chamomilla*) had the tendency to highly take up f cadmium from the soil and *Salvia officinalis* is an excluder of Cd (Marquard and Schneider, 1998).

Helianthus annuus and *Hemidesmus indicus* are Pb hyper-accumulating plants that were used to phytoremediate mines tailings and companies sites polluted with high lead levels in the soil (Boonyapookana *et al.*, 2005; Chandra *et al.*, 2005). The former accumulated in the shoot system while the latter was in both shoot and root systems. Transformation of lead nitrate in the nutrient solution to lead acetate and sulfate occurred in the tissues of *Sesbania drummondii* and take up the metal into roots and aerial parts (Sharma *et al.*, 2004). Anoliefo and Vwioko (1995) noted that used lubricating oil pollution had a stronger effect on *Lycopersicon esculenta* than on *Capsicum annum*. Anoliefo and Edegba (2000) showed that *Solanum melongena* had higher level of tolerance than *S. incanum*. Sharifi *et al.* (2007) also observed that *Medicago truncatula* had the highest tolerance level among the six plant species studied. Cadmium absorb and translocate differently in cultivars of amaranthus (Varalakshmi and Ganeshamurthy, 2009) and radish (Varalakshmi and Ganeshamurthy, 2013). Varalakshmi and Ganeshamurthy (2012) reported high levels of lead in leafy vegetable, then carrot and radish roots, tomato and French bean.

In temperate region, studies confirmed hyper-accumulation of Zn and Cu by *Cardaminopsis helleri* (Neumann and Zur-Nieden, 2001); Cu and Ni by *Empetrum nigrum* (Monni *et al.*, 2000); Cr and Ni by *Echinocloa coIona* (Rout *et al.*, 2000). Peralta-videa *et al.* (2004) revealed the

capability of *Medicago sativa* in cleaning up Cd, Cu and Zn from heavy metals polluted soils. Obilo and Ogunyemi (2005) reported that *Zea mays* bioaccumulated Cd and Pb from crude oil-polluted soil in southeastern Nigeria. According to Schnoor (2002), phytoextraction is more efficient with fast growing plants which are vigorous and can take up high concentration of pollutants in their harvestable form.

2.6. Phytoremediation

Phytoremediation is the removal of pollutants using selected plants species, which resist pollutants, or can take up large quantity of these pollutants and promote reclamation of contaminated sites (Bizly *et al.*, 2000; Lasat, 2002; Zulfqar *et al.*, 2012). During phytoremediation, plants accumulate the pollutants and they either degrade to less harmful forms or uptake them into plant tissues. Thus, this technique is an environmentally friendly and cost-effective technology. More phytoremediators are required particularly under different environmental conditions. For trace elements phytoremediation, two methods involved are phytoextraction and phytostabilization.

Phytoextraction is a method of phytoremediation whereby heavy metals are removed from the soils using plants that are capable to accumulate these metals and translocate them to their aboveground tissues and remediate the soils (Favas *et al.*, 2014; Lai *et al.*, 2015). Plants that are useful for phytoextraction must possess the ability to absorb and tolerate high level of the specific metal, be easy to grow, have a fast growth rate and be resistant to diseases and pests (Gosh and Singh, 2005; Yoon *et al.*, 2006; Ali *et al.*, 2013). These plants are named as phytoextractors or accumulators (Bolan *et al.*, 2014) The quantity of metals removed from the soil is influenced by the crop type used, but soil type and climatic condition of the region (Zhao

et al., 2011). The techniques involved and purposes of phytoaccumulation remain unknown. Higher metal contents in the aerial parts compared to the roots, may be an ecological function resulting to defence against insect, herbivore or fungal attack, thus rendering the aerial parts inedible (Paz-Ferreiro *et al.*, 2014).

On the basis of metal bioavailability, plants are considered as hyperaccumulators, accumulators, indicators, and excluders (Adriano, 2001). The properties and mobility of each metal affect its bioavailability in plant tissues (Tlustos *et al.*, 2006). Heavy metal transportation involves processes like accumulation, storage, metal mobility in the tissue, and restriction of movements within the plant tissue and organelles (Kabata-Pandias and Pendias, 2001). Excluders are plants which are able to thrive in soils with high levels of heavy metals by adopting survival method of maximum exclusion of heavy metals (HM) ions from the plant. Excluder take up HM from the soil and restrict their movements to the roots where the metals are being detoxified while the shoot remain unaffected. On the contrary, accumulators are plants which are capable to take up and keep high level of heavy metals in their aerial parts when exposed to these heavy metals. (Baker, 1981; Rascio and Navari-Izzo, 2011; van der Ent *et al.*, 2013).

The bioconcentration factor (BCF) is a model that shows the capability of plants to take up contaminants from the soil. However, the translocation factor (TF) is shows the heavy metals transfer from plant roots to aerial parts (Mellem *et al.*, 2012; Varun *et al.*, 2012). Plants with bioconcentration and translocation factors >1 are known as accumulators (Usman *et al.*, 2013). Bioconcentration values > 2 are regarded to be high values (Mellem *et al.*, 2012). Plants with high BCF like greater than 20 and biomass yield of $10 \text{ t} \cdot \text{ha}^{-1}$ or with BCF of 10 and biomass yield of $20 \text{ t} \cdot \text{ha}^{-1}$ are required (Peuke and Rennenberg, 2005). Plants with BCF and TF values

higher than one are recommended for phytoremediation, and are mainly for phytoextraction (Fitz and Wenzel, 2002; Yoon *et al.*, 2006).

Phytostabilisation is another phytoremediation technique which involves immobilization of pollutants and containment of metals in the underground biomass (Evangelou *et al.*, 2015; Ogunkunle *et al.*, 2016). The prevention of water erosion and leaching by the plant roots leads to the restriction of heavy metals movement. Precipitation, root adsorption or absorption, reduction of metal valency are mechanisms involved in phytostabilisation. Phytostabilisation primarily focuses on heavy metal sequestration in the roots. Plants with BCF values greater than 1 and TF values less than one are appropriate for phytostabilization (Yoon *et al.*, 2006; Mendez and Maier, 2008; Garba *et al.*, 2013). Plants with BCF values that lack the efficiency to translocate heavy metals to the aerial parts are suitable for phytostabilization (Nirola *et al.*, 2015; Mahajan and Kaushal, 2018).

2.7. Biochar and phytoremediation

There are several reports on soil amendments, such as lime and compost for reduction of heavy metals bioavailability (Komárek *et al.*, 2013) thereby being used together with phytoremediating plants (de Abreu *et al.*, 2012). From previous reports, biochar has the ability immobilize heavy metals and stabilise these heavy metals in soils. In several reports, biochar was revealed to increase plant growth, therefore has the capacity to increase the yield of plants used for remediation (Wu *et al.*, 2019). However, until recently there was not enough experiments on the combined approaches to soil remediation.

Soil properties such as soil pH, nutrient content or SOM can be enhanced to improve metal accumulation. Regarding to this, agricultural practices can be done to reduce plant stress in high

heavy metal contaminated soil (Adriano *et al.*, 2004; Gabos *et al.*, 2011; de Abreu *et al.*, 2012). Liming can reduce the availability of heavy metal, hence improve vegetative growth. Liming and fertiliser application is able to disrupt the movement and speciation of heavy metals in the soil. For effective phytoremediation through liming, the type of amendment to be used must be carefully selected because cations related to the phosphate may alter the heavy metal movement (Bolan *et al.*, 2003; Huang *et al.*, 2013).

Introduction of these combined approaches result to increase in water and mineral retention, boosting of soil pH. The efficiency of particular biochars will further depend on soil properties (Ahmad *et al.*, 2014), the targeted heavy metals (Beesley *et al.*, 2011), and differences in plant species such as differences in their root growth patterns and in their capacities to uptake and accumulate heavy metals (Rizwan *et al.*, 2016). Ideally, biochar derived from organic materials possess the capacity to enhance crop yield and hence being utilized in conjunction with phytoremediation. Biochar and phytoremediation techniques was used by Houben *et al.* (2013) on *Brassica napus L.* at Cd-polluted soils in combination with Miscanthus biochar but for multicontaminated soils, various biochars and plant species were used (Fellet *et al.*, 2014).

From the work of Houben *et al.* (2013), *Brassica napus* was hindered from phytoextracting cadmium and zinc in pots with biochar due to the lower BCF resulting from metal reduction by biochar. They suggested that biochar and *Brassica napus* could be a substitute for phytostabilising heavy metals. Fellet *et al.* (2014) reported that plants grown with biochar derived from fig tree exhibited higher concentrations of Pb. Therefore, biochar and phytoremediation methods can be combined to improve heavy metal contaminated soils. Biochar can reduce the heavy metals bioavailability in the soil. Moreover, phytoextractors is able to lower the level of heavy metals in contaminated sites (Paz-Ferreiro *et al.*, 2014). Nirola *et al.*

(2016) reported *Acacia pycnantha* as a tolerant plant for copper. Takarina *et al.* (2017) reported that *Rhizopora sp.* is a potential phytoextractor of Zn and Pb. They further revealed that *Avicennia sp.* Showed the potential to bioaccumulate Cu as well as phytoextract Pb and Zn.

2.8. Selected plants for the study

Pennisetum glaucum (L.) R. Br. (Pearl millet) is a cross-bred monocot belonging to the family Poaceae. It is consumed by humans as food due to its high nutritional qualities (Yadav *et al.*, 2016). The grains serve as feed for poultry and livestock. The straw is used for bedding, thatching, fencing and fuel. Researches have been conducted on phytoremediation potential of *Pennisetum glaucum* and has been confirmed to be a good phytoextractor of some heavy metals like cadmium and lead (Bareen *et al.*, 2012; Wuana *et al.*, 2013). There has not been much research on the response of *Pennisetum glaucum* to the exposure of heavy metal in soil and its phytoremediation potential in response to amendment agents such as biochar.

Zea mays L. known to be the only species, belongs to the tribe Maydeae and is the most essential cereal that is broadly spread all over the world after wheat and rice. *Zea mays* is an annual and fast-growing cereal (Ahamefule *et al.*, 2014). It serves as the major food fit to be consumed by human, as forage for animals and as natural materials for industrial usage. Maize thrives well on a great variety of soils, but grows better on well drained, aerated, deep, loamy soil rich in sufficient organic matter and provided with available nutrients in neutral to mildly alkaline reaction (Nafziger, 2014). From previous studies, it has been revealed that this plant could have the potential to remediate soil polluted with inorganic pollutants (Wuana and Okieimen, 2010).

Tridax procumbens is a perennial plant which belongs to the family Asteraceae and is available in all seasons. *Tridax procumbens* is known as a widespread weed with massive root system and

rapid growth rate. The plant is a prostrate herb that is beneficial due to its medicinal properties (Mir *et al.*, 2016). Recently, it was confirmed that some plants that have pharmaceutical properties responded to the changing environmental conditions and can generate specific secondary metabolites involved in detoxification of toxic metals. Therefore, they can also play important role in phytoremediation technologies (Masarovičová and Král'ová, 2007; Kumar *et al.*, 2015). Research on *T. procumbens* confirmed the plant as a good weed species for phytoremediation and restoration of land contaminated toxic metals (Kumar *et al.*, 2013; Kale and Deshmukh, 2014).

Tithonia diversifolia (Mexican sunflower) is a fast growing and widely distributed weed native to Central America but now found in many tropical countries including Nigeria. According to Agboola and Adeoye (2005), *T. diversifolia* is now widely distributed in the southern part of Nigeria, particularly, the southwestern and the coastal regions. It was used to boost soil fertility and plant yield in some African countries (Orwa *et al.*, 2009; Adejumo *et al.*, 2011). It serves as ornamental plant and feed for animals and the leaves can be used as medication for constipation, stomach pain, sore throat (Orwa *et al.*, 2009). Adewole *et al.* (2008) reported *T. diversifolia* as a weed capable of surviving in polluted sites.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study site

The potted experiment was set up during the dry seasons of 2018 and 2019 in the Botanical Garden of the University of Ilorin, Ilorin, Kwara State, Nigeria. The University of Ilorin Botanical garden lies between latitude 08° 28'N and longitude 04° 40 E and latitude 8.500 °N and longitude 4.550 °E. The annual rainfall in the area is about 1200 mm and temperature varies between 33°C and 34°C during the year, with a distinct dry season from December to March.

3.2 Collection of materials

Top soil (0-15 cm deep) was collected with a steel shovel from the surroundings of Botanical garden, University of Ilorin, Ilorin, Kwara State. Polyethylene pots were obtained from Niger River Basin, Ilorin, Kwara State. The spent engine oil was collected from Mandilas, a Toyota Automobile Company located in Ilorin, Kwara State. The specifications of the spent oil are as follow:

Grade: SAE20W-50 **Product name:** Visco2000 **Maker:** Forte Oil PLC

Car Brand: Toyota **Age:** Between 1-10 years **Mileage:** 5000km

One commercial biochar (standard) (Wheat straw, 700 °C) and two locally produced biochars (Rice straw, 550 °C and Sorghum straw, 550 °C) were used. The commercial grade biochar (Wheat straw, 700°C) was obtained from UK Biochar Research Centre (UKBRC). Rice and

sorghum straw were collected from Rice farm, Patigi, Kwara State and Sorghum farm, Ilorin, Kwara State respectively.

Seeds of *Tithonia diversifolia* and *Tridax procumbens* were collected from Botanical garden, University of Ilorin, Ilorin, Kwara State and seeds of *Pennisetum glaucum* and *Zea mays* were collected from the National Centre for Genetic Resources and Biotechnology (NACGRAB) Moor Plantation, Ibadan, Oyo State.

3.3 Biochar production

Biochar was generated using slow pyrolysis which was carried out at the Institute of Engineering, Kwara State Polytechnic, Kwara State. Prior to pyrolysis, rice and sorghum straw were crushed and air-dried for easy pyrolysis. Pyrolysis was conducted by batch operation as illustrated by Garcia-Perez *et al.* (2010). Feedstocks were weighed into a cylindrical steel reactor (diameter of 39.80 cm and length of 58 cm) and heated by using charcoal in pit furnace. This was done at 550°C for 3 hours. The temperature was monitored by non-contact digital Infrared thermometer (LHTH, model number – DT8380) at a distance-to-spot ratio of 8:1. The derived biochars cooled down to room temperature overnight and were removed before preparing the reactor for the next batch.

The commercial biochar (wheat straw) was produced by the UKBRC, Edinburgh, United Kingdom. As described by the manufacturer, the biomass was subjected to thermal pyrolysis in a pilot-scale rotary kiln unit at 700°C for 5 minutes. All biochars were lightly crushed and sieved through < 2 mm mesh size.

3.4 Biochar characterization

3.4.1 Physical properties

3.4.1.1. Production yield

Production yield of biochar was determined using the formular below:

$$\% \text{ production yield} = (M_{\text{biochar}}/M_{\text{raw material}}) \times 100$$

where $M_{\text{bio-char}}$ and $M_{\text{raw material}}$ is the mass of biochar and raw material, respectively (Zhang *et al.*, 2015).

3.4.1.2 Internal surface morphology and porosity

These were determined using Scanning Electron Microscope (SEM) following the procedure of Yadav *et al.* (2016). Biochar was mounted on aluminum stubs with double-sided carbon coated sputter coating with gold palladium (Elko IB-3 Ion Coater). The biochar was investigated at varying magnifications with use of JEOL (JSM-6390LV) scanning electron microscope (SEM) that was operated at 10-15kV accelerated voltage.

3.4.2. Chemical properties

3.4.2.1 Determination of pH

The pH of the biochars were determined using the procedure of Rajkovich *et al.* (2011). The biochar (1 g) was weighed into 20 ml deionized water on the shaker and shaken for 90 minutes to establish adequate equilibration between the water and biochar surfaces. pH meter (PHS-3C) was used to determine the pH reading of the biochar.

3.4.2.2 Determination of moisture content

This was determined following the procedure of ASTM D1762 (1990). The muffle furnace was heated to 750°C with ignited porcelain crucibles for 10 mins. The crucibles were placed in a desiccator for 1 h to cool and were weighed with 1 g of each ground biochar. The biochar was placed in the oven at 105°C for 2 h. Each dried biochar was placed in a desiccator for 1 h and weighed. Moisture content was calculated using the formula below:

$$\text{Moisture content (\%)} = (A - B/A) \times 100$$

where: A = mass of air-dried sample used, and B = mass of sample after drying at 105°C

3.4.2.3 Determination of volatile matter

The volatile matter was determined according to ASTM D1762 (1990) method. The muffle furnace was heated to 950°C. The crucibles with biochar used for the moisture determination was preheated. The furnace door was opened, for 2 min on the outer edge of the furnace at 300°C and then for 3 min on the edge of the furnace at 500°C. The crucibles were moved to the rear of the furnace for 6 min with the muffle door closed. The biochar was cooled in a desiccator for 1 h and was weighed. Volatile matter was calculated using the formula below:

$$\text{Volatile matter (\%)} = (B - C/B) \times 100$$

where, C = mass of sample after drying at 950°C, B = mass of sample after drying at 105°C

3.4.2.4 Determination of ash content

The ash content was determined using ASTM D1762 (1990) method. The crucible with biochar content used for the volatile matter determination was placed in the muffle furnace at 750°C for

6 h. The biochar was cooled in a desiccator for 1 h and weighed. Ash content was calculated using the formula below:

$$\text{Ash (\%)} = (D/B) \times 100$$

where, D = weight of residue after drying at 750°C, B = mass of sample after drying at 105°C

3.4.2.5 Determination of fixed carbon

This was determined by subtracting the summation of volatile matter value (VM) and ash content value from 100 (Fabbri *et al.*, 2012).

$$\text{Fixed Carbon} = 100 - (\text{VM} + \text{Ash content})$$

3.4.2.6 Elemental analysis

The elements present in each biochar sample was determined using Energy Dispersive X-ray analyzer (Thermo Electron Corporation, 6733B-IUUSN, USA) which was coupled to the SEM. Electron images were captured using Noran system six imaging software (Stella-Mary *et al.*, 2016).

3.4.3 Functional properties

3.4.3.1 Determination of the surface functionality

The surface functionality of each biochar was determined according to the method of Yadav *et al.* (2016). Each biochar was mixed with KBr in a ratio of 1:200 (w/w) and pelletized using a hydraulic press under constant pressure and further analysed using Fourier Transform Infrared Transmission Spectroscopy (FTIR). Perkin-Elmer Universal ATR sampling accessory spectrum

100 FT-IR Spectrophotometer was used to observe the vibrations of samples and the IR spectra was recorded at room temperature (298 K) in the region 4000–400 cm^{-1} and 1.0 cm^{-1} resolution. The peaks obtained were interpreted as described by John Coates (2000) as follow:

Peaks	Functional groups	
3400-3200	Normal “polymeric” OH stretch	O-H stretch
2935-2915	Methylene (CH_2) Methylene C-H asymmetric	C-H stretch
2800-2700	Aldehyde	C-H stretch
2260-2190	Alkyne (disubstituted)	$\text{C}\equiv\text{C}$ stretch
2100-1800	Transition metal Carbonyls	C-O stretch
1650-1600	Conjugated double bond of Quinone and Ketone	$\text{C}=\text{C}$ stretch
1420-1300	Carboxylic acid salt	C-O stretch
1410-1310	Phenol or Tertiary alcohol OH bend	O-H bend
1050	Primary alcohol	C-O stretch
900-670	Aromatic C-H out of plane bend	C-H bend
700-600	Aliphatic Bromo Compounds	C-Br stretch
660-630	Thioethers $\text{CH}_3\text{-S-}$ and Alkyne C-H bend	C-S Stretch
600-500	Aliphatic Iodo Compounds	C-I stretch

3.4. Spiking of soil

Sandy loam soil was bulked and homogenised to give one representative sample of approximately 300 kg. The soil was sieved through a mesh size of 2-mm to retain the soil free of unwelcome substance that may disrupt soil micro-organisms activities and their functions. Following the method of Adu *et al.* (2015), the sieved soil was air-dried before weighing so as to keep away from apparent weight of soil that could result from the weight of water. Through this method, an accurate weight of soil was gotten in respect to the engine oil used.

Preliminary test was carried out such that soil was spiked with different concentrations (2.5%, 5% and 10%) of spent oil to evaluate the degree of pollution. The fraction of 5% was chosen based on the result of the test carried out. The soil was spiked with spent engine oil with fraction of 50 ml/kg (5 % v/w). In a thorough manner, the soil was mixed with hand protected with gloves and was left for two weeks in a humid environment in the garden (Houben *et al.*, 2013). This was done for uniformity of oil and the soil properties, and proper soil micro-organisms activities. The soil was sampled for laboratory analysis and air dried for 2 days at room temperature.

3.6 Amendment of soil with biochar

Polluted soil was thoroughly mixed with 1%, 2% and 3% of biochar. According to International Biochar Initiative (IBI) guideline, application rate of 2.5% equivalent to 50t/ha was used. This application rate is equal to a field application rate from 5-50t/ha recommended by International Biochar Initiative (IBI) based on an assumption of 2000t/ha. Polyethylene pots (19 cm diameter

and 23 cm height) were filled each with 3 kg of the amended soil. Following Jien and Wang (2013) method, amended soil was thoroughly homogenized and tap water was added to approximately 60% water holding capacity (i.e., the field water capacity of the soil). The pots were left for a month in a humid environment in the garden and weighed every 3 days for maintenance of constant moisture content. Each treatment was in triplicates.

3.7 Determination of soil parameters

3.7.1 Physical properties

3.7.1.1 Determination of porosity

This was determined by saturation method (Ambarsht, 1986). The spiked and amended soil sample was measured in a graduated cylinder and was recorded as volume of the sample (V_s). A measured amount of water was poured into the beaker and was also recorded. Soil sample was saturated with the measured water. Volume of water used (V_p) was subtracted from the starting volume of the graduated cylinder. Porosity was calculated as

$$\text{Porosity} = \text{pore volume} / \text{total volume} \times 100$$

$$\text{Total volume} = V_s + V_p$$

where V_s = Sample Volume, V_p = Pore Volume

3.7.1.2 Determination of water holding capacity

The water holding capacity of the soil was determined according to the method of Ambarsht (1986). Filter paper was placed in the funnel attached to a graduated cylinder and 100ml of spiked and amended soil was measured into the funnel. Water (100ml) was measured with

graduated cylinder. The water was added to the spiked and amended soil sample until it was covered, stirred and left until fully saturated. The amount of water added was recorded. Excess water was collected from the graduated cylinder and was recorded. Water holding capacity was calculated using the formula below

$$\text{Water retained} = \text{water added (ml)} - \text{water drained (ml)}$$

$$\text{Water holding capacity} = 10 \times (\text{ml water retained} / 100 \text{ ml sample})$$

3.7.2 Chemical analysis

3.7.2.1 Determination of pH

The pH of the spiked and amended soil was determined according to the method of Rajkovich *et al.* (2011). The spiked and amended soil (1 g) was weighed into 20 ml of deionized water on the shaker and shaken for 90 minutes to establish adequate equilibration between solution and soil surfaces. pH meter (PHS-3C) was used to determine the pH reading of the soil.

3.7.2.2 Determination of moisture content

This was determined according to the method of ASTM D1762 (1990). The muffle furnace was heated to 750°C with ignited porcelain crucibles and placed in the furnace for 10 mins. The crucibles were placed in a desiccator for one hour to cool, weighed and 1 g of the spiked and amended soil was added. The spiked and amended soil was placed in the oven at 105°C for 2 h. The dried soil sample was placed in a desiccator for 1 h and was weighed. Moisture was calculated using the formula below:

$$\text{Moisture (\%)} = (A - B/A) \times 100$$

where: A = mass of air-dried spiked and amended soil sample used, and B = mass of spiked and amended soil sample after drying at 105 °C

3.7.2.3 Determination of organic matter

This was determined by loss of Ignition (Reddy *et al.*, 2009). Each spiked and amended soil sample (1 g) dried at 105°C was weighed into a crucible. The weight of the crucible with soil sample was taken before ignition. Each soil (spiked and amended) sample was subjected to heat at 550 °C for 24 hours and weighed again after the temperature dropped to 105 °C. Percentage organic matter was calculated using the following formula;

$$\text{Loss of ignition} = \frac{\text{weight at 105 } ^\circ\text{C} - \text{weight at 550 } ^\circ\text{C}}{\text{weight at 105 } ^\circ\text{C}} \times 100$$

3.7.2.4 Mineral content determination

The official method of AOAC (2005) was adopted. The spiked and amended soil samples were ashed in a furnace for 5 h at 600°C, and then boiled with 10 ml of 20% hydrochloric acid in a beaker. The mixture was filtered into a 100 mL standard flask and was made up to the mark with deionized water. Potassium (K) level of the soil sample was determined using Flame Emission Photometer with KCl as standard. All other metals were determined by Atomic Absorption Spectrophotometer (AAS Model Bulk Scientific Accuzy 211).

3.7.2.5 Heavy metal determination

The method of Thompson and Wood (1982) was adopted. One gram of the spiked and amended soil samples were digested in 4:1 ratio of concentrated 69% HNO₃ (Analar grade) and

concentrated 60% HClO₄ (Merck, Germany). The mixtures were heated to dryness. Each residue was then leached with 5 M of 36% HCl (Analar grade) and filtered through a Whatman No. 41 filter paper. The filtrate was finally diluted with distilled water to 1M HCl. The samples were analysed for heavy metals including Cd, Cu, Pb, Ni and Zn by Atomic Absorption Spectrophotometer (AAS model 210VGP, Buck Scientific Incorporated USA) with Air-Acetylene flame. Procedural blanks were carried out and samples in triplicate to validate the accuracy of the procedure.

3.8 Planting and harvesting

3.8.1 Seeds for planting

The seeds of *Zea mays*, *Pennisetum glaucum*, *Tridax procumbens* and *Tithonia diversifolia* were collected and were sowed. The choice of these plants was based on their availability and tolerance to unfavourable conditions as reported from previous works.

3.8.2 Planting preparation

Viability tests were conducted on the seeds with floatation method. Ten (10) viable seeds of *Zea mays*, *Pennisetum glaucum*, *Tithonia diversifolia* and *Tridax procumbens* were sowed per pot. The numbers of germinated plants were thinned to two plants per pot. Watering was done daily with 180 ml of tap water and regular weeding was done by hand picking. The experiment was arranged in a complete randomized design for a discrete and perfect result.

3.8.3 Harvesting

The plants were harvested six (6) weeks after planting. The shoot biomass was collected from the base of the plant stalks. The root biomass was manually separated from the potted soil and washed off soil and biochar particles (Rajkovich *et al.*, 2011).

3.9 Morphological growth characters

3.9.1 Plant height

One plant was selected from each pot for the measurement of plant height. Plant height was measured by determining the height of the plant from the soil level to the collar of the uppermost leaf (Okonokhua *et al.*, 2007). Plant height was recorded weekly.

3.9.2 Number of leaves

This was done by counting the leaves per plant in each pot. Number of leaves was recorded weekly.

3.9.3 Leaf area

Leaf area was determined by measuring the length and width (at the widest point) of a leaf per plant. The products of the length and width were multiplied by a correction factor of each plant. The correction factors of the plants are as follows: *Zea mays* and *Pennisetum glaucum* (0.75); *Tithonia diversifolia* and *Tridax procumbens* (0.79) (Watt, 1973). Leaf area was recorded weekly.

3.9.4 Stem girth

Stem girth of a plant per pot was measured with thread which was later extrapolated on the ruler. Stem girth was recorded weekly.

3.9.5 Root length

Root length of a plant per pot was measured with thread which was later extrapolated on the ruler. Root length was measured after harvesting of plant.

3.9.6 Fresh weight of plant

A plant was selected per pot and the fresh weight was measured on a calibrated weighing balance immediately after harvest.

3.9.7 Dry weight of plant

A plant per pot was selected and air dried to constant weight and weighed on a calibrated weighing balance after harvesting.

3.10 Heavy metal determination

The method of Thompson and Wood (1982) was adopted. One gram of each plant sample was digested in 4:1 ratio of concentrated 69% HNO_3 (Analar grade) and concentrated 60% HClO_4 (Merck, Germany). The mixture was heated to dryness. The residue was then leached with 5 M of 36% HCl (Analar grade) and filtered through a Whatman No. 41 filter paper. The filtrate was finally diluted with distilled water to 1M HCl . The samples were analysed for heavy metals including Cd, Cu, Pb, Ni and Zn with Atomic Absorption Spectrophotometer (AAS model

210VGP, Buck Scientific Incorporated USA) with Air- Acetylene flame. Procedural blanks were carried out and samples in triplicate to validate the accuracy of the procedure.

3.11 Plant-soil relationship

The mobility of the heavy metal from the contaminated soil into the plant roots and the ability to mobilise the metals from roots to aerial parts were examined correspondingly by means of Bio-concentration Factor (BCF) and the Translocation Factor (TF) models.

3.11.1 Bio-concentration factor

This is a model used to check the ability of plant to take up and store a specific metal with respect to its concentration in the soil (Ghosh and Singh, 2005). Bio-concentration factor (BCF) was calculated as a ratio of heavy metal concentration in plant roots to the heavy metal concentration in soil (Yoon *et al.*, 2006).

$$BCF = C_{\text{metal root}} / C_{\text{metal soil}}$$

where $C_{\text{metal root}}$ and $C_{\text{metal soil}}$ concentration of heavy metal in root and concentration of heavy metal in soil respectively.

BCF values >2 will be regarded as high values which implies better phytoaccumulation capabilities of the plant. The higher the BCF value, the more suitable the plant is for phytoextraction (Blaylock *et al.*, 1997).

3.11.2 Translocation factor (TF)

This is the ratio of heavy metal concentration in plant shoot to that in plant root (Yanqun *et al.*, 2005). This ratio shows the ability of the plant to uptake and move metals from the roots to the shoots of the plant (Marchiol *et al.*, 2004).

$$TF = C_{\text{metal shoot}} / C_{\text{metal root}}$$

where $C_{\text{metal shoot}}$ and $C_{\text{metal root}}$ concentration of heavy metal in shoot and concentration of heavy metal in root respectively. $TF < 1$ shows that the plant is an excluder while $TF > 1$ shows that the plant is an accumulator. $TF = 1$ shows that the plant is an indicator (Olowoyo *et al.*, 2010).

3.12 Statistical analyses

One-way Analysis of Variance (ANOVA) was used to assess the significant differences of the biochar treatments and Duncan's Multiple Range Tests ((DMRT) was used to check the level of the significant differences of biochar treatments based on soil properties, growth parameters and heavy metal content ($p < 0.05$)

CHAPTER FOUR

RESULTS

4.1 Properties of biochar

4.1.1 Physicochemical properties

Table 1 shows the properties of the three different biochars used in this study. Standard biochar at 700°C underwent fast pyrolysis with resident time of 15mins while sorghum and rice biochar underwent slow pyrolysis with resident time of 3hrs. Sorghum biochar had the highest % production yield (36.37%) followed by rice biochar (30.0%) and standard biochar (23.54%). The pH value for rice biochar and sorghum biochar was 8.54 and 8.41 respectively. However, standard biochar had the least pH value (8.15), all were alkaline. Moisture content of sorghum biochar was 5.75% and the least was recorded for standard biochar (3.48%). Rice biochar had the highest volatile matter (21.39%) and the least was found in sorghum biochar (12.55%). Ash content recorded for rice (52.37%) and sorghum biochar (35.07%) were higher than standard biochar (20.13%). Sequence of fixed carbon for the studied biochars are as follow: standard biochar (56.45%) > sorghum biochar (46.63%) > rice biochar (22.11%). Sorghum and rice biochars had the higher O/C (0.24) than standard biochar (0.19) (Table 1).

Table 2 shows the elemental compositions of the studied biochars. Rice and sorghum biochars recorded higher values for the following elements: Oxygen, Magnesium, Potassium, Chlorine, Silicon, Aluminium and Iron than standard biochar. However, standard biochar recorded highest Beryllium (23.39%), Phosphorus (1.69%), Calcium (4.89%) and Carbon (57.57%) (Table 2). The heavy metal content of the studied biochars were significantly lower than the permissible limits

Table 1: Physicochemical properties of the test biochars

Biochars /Properties	Standard biochar	Sorghum biochar	Rice biochar
Temperature (°C)	700	550	550
Resident time	15 min	3 hrs	3 hrs
Production type	Fast	Slow	Slow
Production1 yield (%)	23.54	36.37	30
pH	8.15	8.41	8.54
Moisture (%)	3.48	5.75	4.13
Volatile matter (%)	19.94	12.55	21.39
Ash content (%)	20.13	35.07	52.37
Fixed carbon (%)	56.45	46.63	22.11
O/C ratio	0.19	0.24	0.24

Table 2: Elemental composition of test biochars

Elements	Standard biochar	Sorghum biochar	Rice biochar
Carbon (wt%)	57.57	55.64	53.87
Oxygen (wt%)	10.68	13.57	12.73
Magnesium (wt%)	0.53	0.69	0.70
Calcium (wt%)	4.89	3.80	1.84
Potassium (wt%)	6.64	7.89	11.88
Chlorine (wt%)	0.69	0.96	2.02
Silicon (wt%)	8.15	14.72	14.36
Aluminium (wt%)	0.28	3.81	1.33
Titanium (wt%)	0.00	1.08	0.00
Iron (wt%)	0.00	4.34	4.19
Phosphorus (wt%)	1.69	0.00	0.84
Beryllium (wt%)	23.39	0.00	0.00
Copper (mg/kg)	15.33	23.33	34.00
Zinc (mg/kg)	0.00	1.00	2.33
Lead (mg/kg)	0.00	1.00	1.00
Cadmium (mg/kg)	0.00	4.33	4.00
Chromium (mg/kg)	1.00	3.00	4.00

for Cu (63 – 1500 mg/kg), Pb (70 – 500 mg/kg), Zn (200 - 2800 mg/kg), Cr (64 – 100 mg/kg) and Cd (1.4 – 39 mg/kg) recommended for biochars.

Plate 1 shows the surface morphology of the studied biochars. All the studied biochars exhibited different pore structures. A network of skeletal structure appeared on the surface of the rice biochar (Plate 1a) and various pore structures, that is, both macropores and micropores were present (Plate 1b). Sorghum biochar possessed structure that looks like sieve plate with minute pores of almost same size (Plate 1c) and more of macropores were found on its surface (Plate 1d). For wheat biochar, the micropores were found to be more and skeletal in structure as observed on the surface which revealed the appearance of fractures (Plates 1e and 1f).

Figure 1 shows the surface functionality of wheat biochar (WB) 700°C, sorghum biochar (SB) 550°C and rice biochar (RB) 550°C. The studied biochars were observed to have almost the same functional groups; C-H, C≡C, C=C, C-O, C-X and S-S. For all the studied biochars, there was a band at 2700 cm⁻¹ which was attributed to presence of aldehyde (C-H stretch). A peak was observed at 2200 cm⁻¹ which revealed triple bonds between carbons of Acetylenic compounds (C≡C stretch). There was appearance of a band at 2050 cm⁻¹ which corresponded to transition metal carbonyls and a peak at 1650 cm⁻¹ was observed which revealed the conjugated quinone and ketones (C=C stretch). Observations of peaks at 1050 cm⁻¹ characterized the presence of C-O stretch. Frequency range from 900 cm⁻¹ to 885 cm⁻¹ revealed the peaks corresponding to aromatic compounds (C-H out of plane bend) and a band observed at 570 cm⁻¹ showed presence of halogen (C-X stretch). Moreover, a band observed at 470 cm⁻¹ was attributed to polysulphide (S-S stretch). A peak at 1420 cm⁻¹ was observed in sorghum biochar only and this revealed the presence of carboxylic acid salt (C-O stretch). There was an observation of high peak at 3400 cm⁻¹ in rice and wheat biochar which was ascribed to O-H stretching vibration. In addition,

observation of a band at 1400 cm^{-1} characterized the presence of phenolics (O-H bend). Whereas, in rice biochar only, there was a band observed at 2930 cm^{-1} which symbolized aliphatic CH_2 assymmetric (C-H stretch) and a peak observed at 630 cm^{-1} revealed thioethers (C-S), aliphatic bromo compounds (C-Br) and alkyne (C-H bend).

4.2 Effect of biochar on soil

4.2.1 Soil properties

Table 3 shows the soil properties under different concentrations of different biochars in the two seasons. It was observed that higher values were recorded for the physicochemical properties in year 2019 than in year 2018 except for porosity. In comparison to the control, all the biochar amendments significantly ($p \leq 0.05$) increased the soil porosity except 3% RB treatment for both years. In response to the application of all the biochars, water holding capacity and pH were significantly ($p \leq 0.05$) higher in soils amended with biochars than the control for both years.

In 2018, sorghum biochar (SB) and rice biochar (RB) showed significantly ($p \leq 0.05$) higher moisture content than the control (8.40 ± 2.29) but numerically greater than standard biochar. However, moisture content significantly ($p \leq 0.05$) reduced in soil treated with standard biochar. In 2019, significantly ($p \leq 0.05$) higher moisture content was recorded in soil treated with 1% and 2% standard biochar and sorghum biochar, and 2% and 3% RB when compared to the control. It was observed that rice biochar had the highest moisture content in 2018 and standard biochar recorded the highest in 2019 ($18.15 \pm 5.20\%$). In 2018, standard biochar had significantly ($p \leq 0.05$) higher organic matter than the control soil and other biochar amended soils. Meanwhile, soil amended with all the biochars in 2019 were significantly ($p \leq 0.05$) higher in organic matter

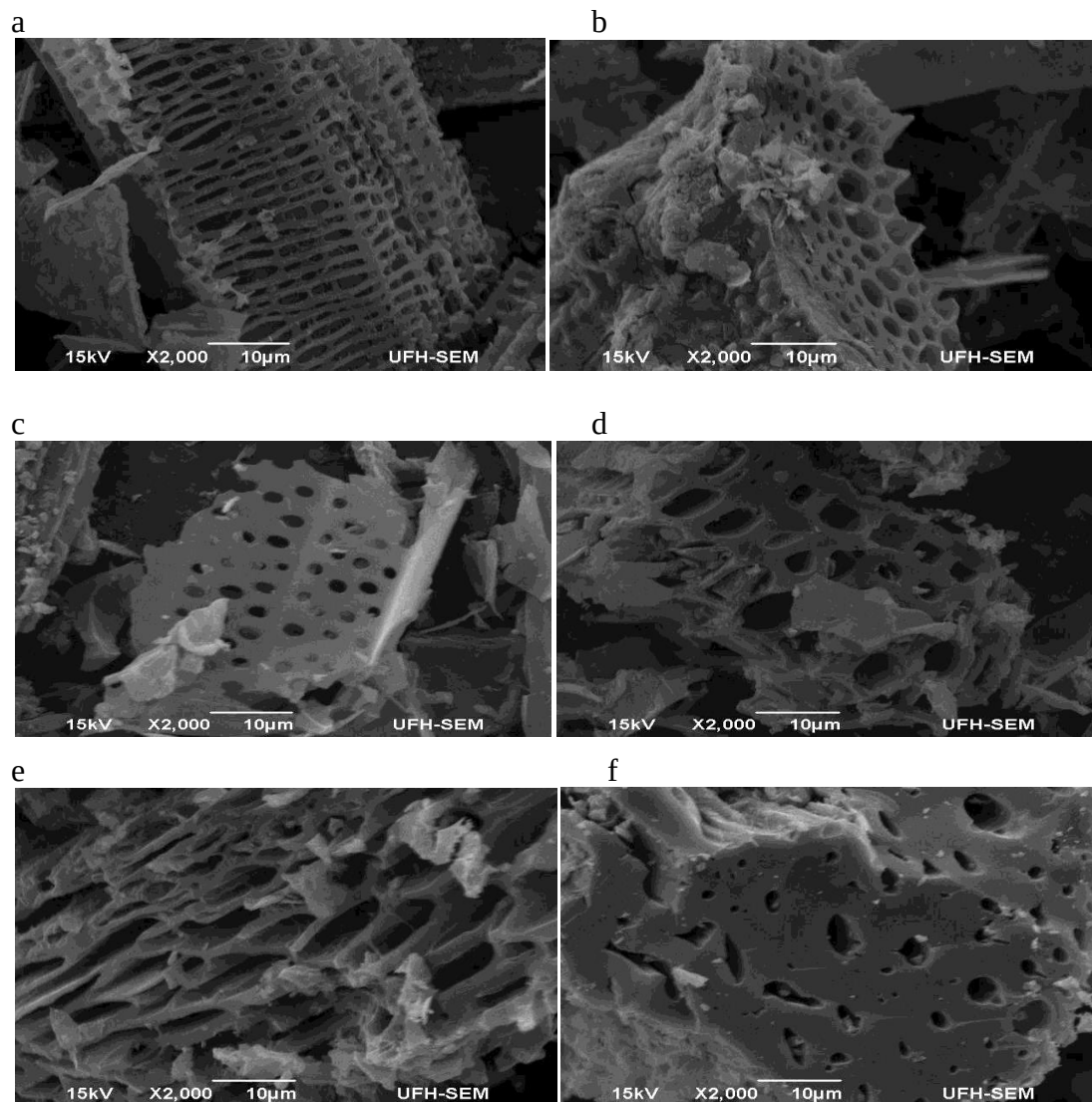


Plate 1: Scanning Electron Micrographs of test biochars

Key: Rice biochar (a and b), sorghum biochar (c and d) and standard biochar (e and f).

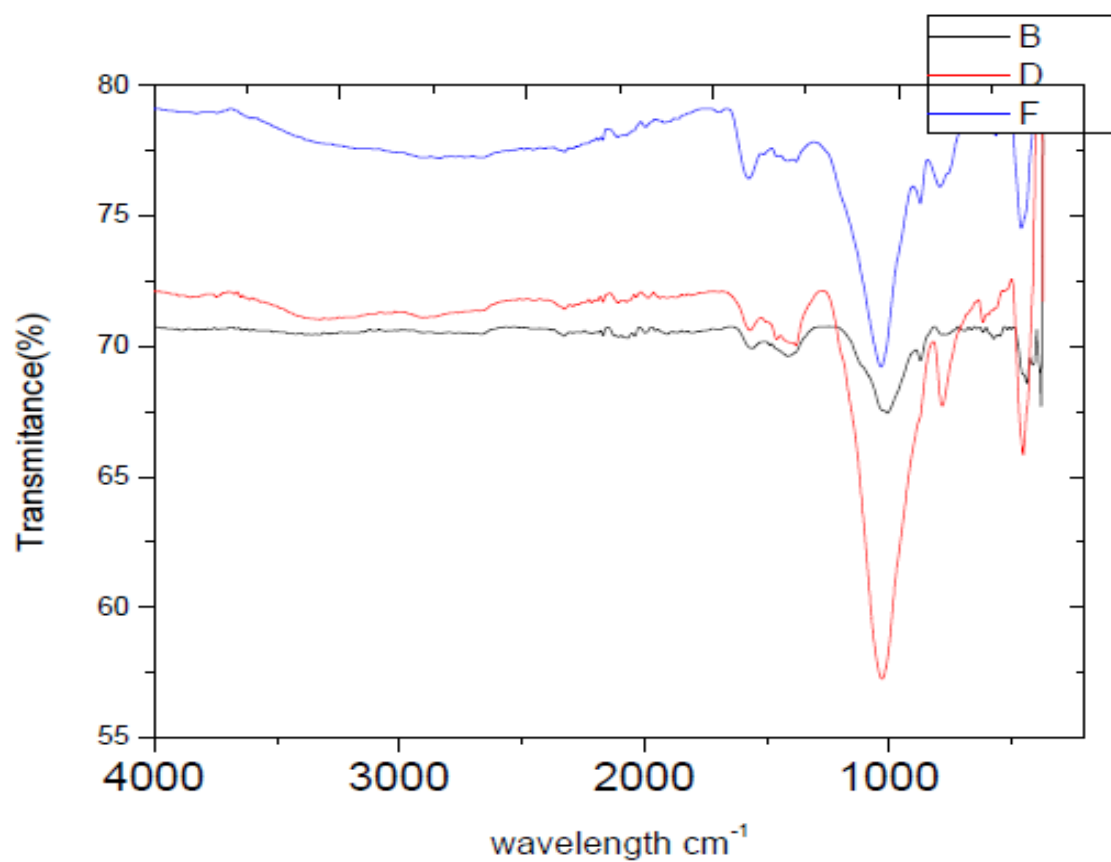


Figure 1. FTIR spectra of sorghum biochar 550°C (B), rice biochar 550°C (D) and standard biochar 700°C (F)

Table 3: Effects of different concentrations of biochars on physicochemical properties of soil in 2018 and 2019

Trts	Rates (%)	2018					2019				
		Porosity (%)	WHC (%)	pH	Moisture (%)	OM (%)	Porosity (%)	WHC (%)	pH	Moisture (%)	OM (%)
Control	0	28.57±0.00 ^f	4.00±0.00 ^c	6.76±0.80 ^d	8.40±2.29 ^{bc}	9.01±1.15 ^b	26.67±0.00 ^f	5.00±1.00 ^c	6.51±0.24 ^c	9.17±1.62 ^d	7.02±0.00 ^e
StB	1	46.21±1.16 ^b	6.00±1.40 ^{abc}	7.20±0.11 ^{cd}	7.28±0.18 ^{cd}	12.11±1.83 ^a	45.83±1.32 ^b	5.66±1.51 ^{bc}	8.60±0.00 ^a	18.15±5.20 ^a	24.00±0.00 ^a
	2	52.13±4.76 ^a	5.23±2.31 ^{bc}	7.20±0.00 ^{cd}	5.54±0.83 ^d	9.74±3.71 ^{ab}	53.72±5.50 ^a	5.26±2.36 ^{bc}	8.46±0.20 ^{ab}	13.10±0.10 ^b	7.80±0.00 ^e
	3	43.45±1.59 ^{bc}	4.70±0.30 ^{bc}	7.10±0.00 ^{cd}	7.65±0.68 ^c	9.86±1.03 ^{ab}	41.57±0.49 ^{bc}	5.03±0.64 ^{bc}	7.56±0.66 ^b	7.82±1.97 ^e	8.38±0.00 ^d
SB	1	34.96±2.53 ^{de}	5.20±1.20 ^{bc}	7.29±0.18 ^{bc}	10.87±0.46 ^a	7.55±1.09 ^b	36.65±1.46 ^d	4.93±0.83 ^d	7.43±0.40 ^b	12.30±1.00 ^b	8.48±1.00 ^d
	2	42.18±1.00 ^c	6.40±0.00 ^{ab}	7.90±0.07 ^a	11.63±0.76 ^a	8.31±0.45 ^b	40.99±0.91 ^c	6.36±0.15 ^{abc}	8.80±0.00 ^a	12.07±4.27 ^b	18.54±0.00 ^b
	3	36.70±0.80 ^d	5.90±1.30 ^{abc}	7.71±0.06 ^{ab}	10.12±0.08 ^{ab}	8.29±0.76 ^b	35.86±0.05 ^d	6.33±1.53 ^{abc}	8.90±0.00 ^a	8.10±0.20 ^d	8.24±0.00 ^d
RB	1	31.70±1.63 ^{ef}	6.10±0.10 ^{abc}	7.26±0.16 ^{abc}	11.82±1.07 ^a	6.79±0.96 ^b	30.07±0.00 ^e	6.76±0.49 ^{abc}	8.50±0.00 ^{ab}	8.02±0.22 ^d	11.33±0.96 ^c
	2	37.22±2.16 ^d	7.60±1.20 ^a	7.92±0.09 ^a	11.08±1.64 ^a	7.38±1.34 ^b	35.78±1.25 ^d	7.53±1.96 ^a	8.90±0.00 ^a	13.22±3.42 ^b	7.59±1.34 ^e
	3	24.80±0.56 ^g	6.60±6.00 ^{ab}	8.04±0.09 ^a	10.94±1.17 ^a	7.71±0.92 ^b	22.12 ±2.85 ^g	7.00±0.34 ^{ab}	8.90±0.00 ^a	10.65±0.10 ^c	11.20±0.92 ^c

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$. **Trts** – Treatments; **StB** – Standard Biochar; **SB** – Sorghum Biochar; **RB** - Rice Biochar; **OM** –Organic matter; **WHC** – Water Holding Capacity

than the untreated soil. Among all the treatments, standard biochar had the highest values of organic matter in both years.

Table 4 shows the effect of biochar on soil nutrient. Biochar treatments increased Fe content in the amended soil as compared to the control in the two seasons. Only soil amended with 2% SB had higher P content than the control soil in 2018 while only soil amended with 3% RB had lower P content than the control soil in 2019. However, the P content of the soil amended with biochars was significantly the same with the control for both years. In 2018, soil amended with StB and 1% RB had higher Ca content than the control soil and soil amended with SB while soil amended with all the biochars had higher Ca contents than the control soil in 2019. In 2018, soil amended with 1% and 2% StB and 3% RB had higher Mg content than the control soil while soil amended with all the biochars had higher Mg contents than the control soil in 2019. In 2018, only soil treated with 3% RB had higher K content while soil amended with biochars had higher K content than the control soil except soil amended with 2% SB and 3% SB.

Table 5 reveals the effect of biochars on heavy metal in the soil. The biochar treatments significantly ($p \leq 0.05$) reduced the heavy metals (Cu, Zn, Pb, Cd and Cr) in the soil when compared to the control. In addition, the heavy metals investigated in the amended soils for both years were lower than the permissible limits. There was a positive response of heavy metals to the biochar percentage interaction for the two years.

Table 4: Effects of different concentrations of biochars on nutrient contents (mg/kg) of soil in 2018 and 2019

Trts	Rates (%)	2018					2019				
		Fe	P	Ca	Mg	K	Fe	P	Ca	Mg	K
Control	0	1.25	0.68	8.27	7.52	3.25	1.40	0.65	2.05	-1.22	2.10
StB	1	1.40	0.66	15.95	17.34	3.12	2.20	0.66	9.66	4.82	2.85
	2	1.55	0.66	11.81	16.11	3.17	1.75	0.68	6.95	2.53	3.13
	3	1.35	0.67	10.66	3.43	3.24	1.70	0.68	9.81	1.96	2.63
SB	1	1.50	0.65	8.99	2.37	2.70	2.10	0.67	10.59	8.42	2.29
	2	1.30	0.69	8.90	6.30	3.11	1.85	0.66	10.20	6.38	1.47
	3	1.40	0.66	7.10	5.89	2.28	2.10	0.65	12.43	3.10	1.24
RB	1	1.40	0.66	12.39	2.78	2.61	2.10	0.65	9.38	2.37	2.18
	2	1.80	0.66	7.08	1.47	2.29	1.90	0.67	9.07	1.71	2.62
	3	1.70	0.67	8.07	9.24	3.54	2.35	0.62	6.40	1.30	3.07

Trts – Treatments; **StB** – Standard Biochar; **SB** – Sorghum Biochar; **RB** - Rice Biochar; Magnesium (Mg), Iron (Fe), Calcium (Ca), Potassium (K), Phosphorus (P). Unit in mg/kg

Table 5: Effects of different concentrations of biochars on heavy metals content (mg/kg) of soil in 2018 and 2019

Trts	Rate (%)	2018					2019				
		Cu	Zn	Pb	Cd	Cr	Cu	Zn	Pb	Cd	Cr
Control	0	129.00±0.00 ^a	0.20±0.00 ^{ab}	0.36±0.05 ^a	0.43±0.05 ^a	5.66±0.57 ^a	35.33±1.15 ^a	1.00±0.00 ^c	0.00±0.05 ^a	0.00±0.00 ^b	5.00±0.00 ^a
StB	1	0.00±0.00 ^e	0.00±0.00 ^e	0.10±0.00 ^b	0.06±0.11 ^{cd}	2.33±0.57 ^c	18.00±0.00 ^d	0.00±0.00 ^d	0.00±0.00 ^b	0.00±0.00 ^b	2.00±0.00 ^{bc}
	2	0.00±0.00 ^e	0.03±0.05 ^{de}	0.06±0.05 ^b	0.13±0.05 ^{bc}	0.00±0.00 ^e	20.00±0.00 ^c	1.00±0.00 ^c	0.00±0.00 ^b	0.00±0.00 ^b	2.00±0.00 ^{bc}
	3	9.66±1.52 ^b	0.10±0.00 ^{cd}	0.13±0.05 ^b	0.10±0.00 ^{bcd}	0.00±0.00 ^e	23.33±2.30 ^b	0.00±0.00 ^d	0.00±0.00 ^b	0.00±0.00 ^b	2.00±0.00 ^{bc}
SB	1	8.00±2.00 ^{bc}	0.23±0.05 ^a	0.13±0.05 ^b	0.16±0.05 ^{bc}	3.33±0.57 ^b	24.00 ±0.00 ^b	0.00±0.00 ^d	0.00±0.00 ^b	1.00±0.00 ^a	2.33±0.57 ^{bc}
	2	6.66±1.15 ^{cd}	0.13±0.05 ^{bc}	0.13±0.05 ^b	0.20±0.00 ^b	2.33±0.57 ^c	23.33±0.00 ^b	0.00±0.00 ^d	0.00±0.00 ^b	0.00±0.00 ^b	2.00±0.57 ^{bc}
	3	7.33±1.15 ^{bc}	0.13±0.05 ^{bc}	0.10±0.00 ^b	0.00±0.00 ^d	3.00±0.00 ^{bc}	18.00±1.15 ^d	0.00±0.00 ^d	0.00±0.00 ^b	0.00±0.00 ^b	2.00±0.00 ^{bc}
RB	1	4.33±0.57 ^d	0.10±0.00 ^{cd}	0.06±0.05 ^b	0.13±0.05 ^{bc}	2.66±0.57 ^{bc}	28.00±0.00 ^b	2.00±0.00 ^b	0.00±0.00 ^b	0.00±0.00 ^b	3.00±0.57 ^b
	2	9.66±1.52 ^b	0.10±0.10 ^{cd}	0.13±0.05 ^b	0.00±0.00 ^d	1.33±0.57 ^d	18.00±0.00 ^d	0.00±0.10 ^d	0.00±0.00 ^b	0.00±0.00 ^b	2.00±0.57 ^{bc}
	3	0.00±0.00 ^e	0.00±0.00 ^e	0.10±0.00 ^b	0.16±0.05 ^{bc}	2.66±0.57 ^{bc}	16.00±0.00 ^e	3.00±0.00 ^a	1.00±0.00 ^b	1.00±0.00 ^a	1.00±0.57 ^d
PL		100	300	50	3	100	100	300	50	3	100
Source of variation		Level of significance									
Biochar percentage		*	*	*	*	*	*	*	*	*	*

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$. **PL** –Permissible Limit (mg/kg) (Source: World Health Organisation, 1996 and 2001). **Trts** – Treatments; **StB** – Standard Biochar; **SB** – Sorghum Biochar; **RB** - Rice Biochar

4.3 Effects of biochars on plant growth

The greatest heights of *Zea mays* (54.38 cm and 70.23 cm) were observed in 3% RB and 3% SB in year 2018 and 2019, respectively (Table 6). In 2018, all the biochar treatments at 5th and 6th weeks had significantly ($p \leq 0.05$) higher plant height than the control. Though, heights of plants treated with 1% and 2% of RB were not determined as a result of death of the plants. However, all biochars at 2% and 3% significantly increased maize height more than the control in 2019. Height of *Z. mays* increased with increase in the concentrations of standard biochar and rice biochar at the end of the experiment in 2018 while there was gradual increase in the height with increased application of standard biochar and sorghum biochar all through the experiment in 2019.

Table 7 reveals no differential effect of the biochars in the number of leaves of *Zea mays*. The 3% RB and 3% SB treatments produced the highest leaf area (59.89 cm² and 90.75 cm²) in year 2018 and 2019, respectively (Table 8). In 2018, all the biochar treatments at 6th week had significantly ($p \leq 0.05$) larger leaf area (51.89 cm²) than the control (14.22 cm²). However, leaf area treated with 1% and 2% of RB were not determined as a result of death of the plants. Meanwhile, standard biochar and sorghum biochar at 2% and 3% had plant leaf area that were significantly ($p \leq 0.05$) larger than the control in 2019. Leaf area increased with increase in the concentrations of rice biochar all through the experiment in 2018 while increased application of standard biochar, sorghum biochar and rice biochar increased the leaf area gradually at weeks 4, 5 and 6 in 2019.

Table 9 reveals that all the biochar treatments recorded stem girth that were significantly ($p \leq 0.05$) greater than the control except 3% SB treatment of *Z. mays* at week 6 in 2018. The 3%

and 2% RB recorded the greatest stem girth (6.60 cm and 3.14 cm) all through the experiment in 2018 and 2019, respectively. Increased sorghum biochar rate resulted in gradual increase in 2019.

Table 10 shows that all biochar treatments recorded heights that were significantly ($p \leq 0.05$) higher than the control at week 4 for *Pennisetum glaucum* in year 2018. At week 5, 2% and 3% standard biochar (StB) amended soil produced *P. glaucum* with height significantly ($p \leq 0.05$) lower than the control. Also, 1% and 2% of StB recorded heights significantly ($p \leq 0.05$) lower than control. The 3% RB concentration had the highest plant height (49.87 cm) at the end of the experiment (week 6). At week 4 of year 2019, 3% of StB and SB produced *Pennisetum glaucum* which were significantly ($p \leq 0.05$) higher than the control. In addition, 1% and 2% of RB also produced *P. glaucum* with higher heights than the control. All biochars at 1% significantly ($p \leq 0.05$) produced plant with lower height when compared to the control at week 5. Moreover, StB and SB at 1% had heights lower than the control. However, height of *P. glaucum* increased with increase in the concentrations of sorghum biochar in both seasons. *Pennisetum glaucum* sowed on 3% StB, 2% and 3% SB and 1%, 2% and 3% RB amended soil were taller than those on the control (Table 10).

Variations were observed in the leaf number of *P. glaucum* (Table 11). In 2018, there was an increase in leaf number with increase in the concentrations of standard biochar and sorghum biochar while rice biochar effects were contrary. In 2019, revealed increase in the leaf number as the biochar treatment increased was observed.

Table 12 shows that only 2% StB treatment reduced the leaf area of *P. glaucum* when compared to the control leaf area at week 4 in 2018. Leaf area of *P. glaucum* raised 3% SB and RB

amended soils significantly ($p \leq 0.05$) larger than the control at week 5 in 2019 (Table 12). All 3% biochar treatments produced leaf areas that were significantly ($p \leq 0.05$) larger than the control at week 6 in 2018. In 2019, leaf area was found to increase as the biochar concentrations increased at the end of experiment. At week 4, only 1% StB treatment increased the leaf area of *P. glaucum*. The leaf areas of *P. glaucum* on 3% of SB and RB at week 5 were larger than the control. At week 6, 2% and 3% SB and RB had leaf areas of *P. glaucum* that were significantly ($p \leq 0.05$) higher than the leaf area of *P. glaucum* raised on the control soil.

Stem girth of *P. glaucum* were significantly ($p \leq 0.05$) higher than all the biochar treatments all through the experiment in the first season (Table 13). In 2019, 3% SB treatment significantly ($p \leq 0.05$) increased the stem girth than the control at week 4. At week 5, 2% and 3% SB and RB possessed significantly higher stem girth than the control. (Table 13). All biochars at 2% and 3% increased the stem girth of pearl millet.

Table 14 shows that the height of *Tithonia diversifolia* decreased with increase in the concentrations of StB and increased with increase in rice biochar concentrations at week 6 in 2018. Rice biochar (3%) and sorghum biochar (3 %) amended soil produced *T. diversifolia* with the higher heights, 13.37 cm and 11.00 cm in 2018 and 2019 respectively. In RB treated soil, *Tithonia* plants were taller than the control in 2018. However, the StB amended soil produced the shortest *Tithonia* plants in 2018. The heights of *Tithonia sp* were shorter in 2019 than in 2018. *Tithonia* plant raised on rice biochar (3%) amended soil had the tallest plant (13.37 cm) all through the experiment.

Table 6: Effects of different concentrations of biochars on height (cm) of *Zea mays* in 2018 and 2019

Trts	Rates (%)	2018			2019		
		Week 4	Week 5	Week 6	Week 4	Week 5	Week 6
Control	0	18.60±3.72 ^{ab}	23.81±1.55 ^b	29.96±1.96 ^b	35.08±3.95 ^{bc}	45.52±5.10 ^a	57.09±6.00 ^{bc}
StB	1	13.81±1.75 ^b	31.62±0.65 ^b	32.72±4.06 ^b	27.63±2.65 ^d	27.56±2.50 ^c	25.57±4.50 ^e
	2	25.6±6.54 ^{ab}	31.17±5.83 ^b	36.36±11.06 ^b	42.24±2.75 ^a	44.01±1.50 ^a	58.00±4.00 ^{bc}
	3	15.94±3.15 ^b	27.54±0.86 ^b	38.38±1.96 ^b	43.87±5.15 ^a	48.24±1.75 ^a	54.92±3.20 ^{bc}
SB	1	20.23±6.37 ^{ab}	28.97±5.48 ^b	35.93±3.85 ^b	29.75±0.75 ^{cd}	27.09±3.00 ^c	29.08±5.45 ^e
	2	28.41±14.05 ^{ab}	44.41±4.70 ^a	48.76±8.61 ^a	34.72±1.25 ^{bc}	44.20±3.75 ^a	61.58±2.95 ^b
	3	20.52±5.49 ^{ab}	27.43±2.19 ^b	35.07±1.46 ^b	34.84±0.70 ^{bc}	47.24±0.75 ^a	70.23±1.75 ^a
RB	1	17.44±6.81 ^{ab}	27.02±2.48 ^b	ND	28.18±1.75 ^d	28.26±1.75 ^c	27.84±1.20 ^e
	2	24.90±17.71 ^{ab}	36.77±17.30 ^{ab}	ND	38.09±6.45 ^{ab}	47.08±1.50 ^a	52.76±5.05 ^{cd}
	3	33.33±3.51 ^a	47.52±8.69 ^a	54.38±0.00 ^a	36.35±2.20 ^b	39.13±1.85 ^b	46.22±2.45 ^d

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$. **Trts** – Treatments; **StB** – Standard Biochar; **SB** – Sorghum Biochar; **RB** - Rice Biochar, **ND**- Not determined

Table 7: Effects of different concentrations of biochars on leaf number (cm) of *Zea mays* in 2018 and 2019

Trts	Rates (%)	2018	2019				
		Week 4	Week 5	Week 6	Week 4	Week 5	Week 6
Control	0	3.00±0.00 ^a	4.00±0.00 ^c	4.00±0.00 ^a	4.00±0.00 ^a	3.00±0.00 ^c	4.00±1.00 ^c
StB	1	3.00±0.00 ^a	4.00±0.00 ^c	3.00±0.00 ^a	3.00±1.00 ^b	4.00±0.00 ^b	4.00±0.00 ^c
	2	4.00±0.00 ^a	4.00±1.00 ^c	3.00±0.00 ^a	4.00±0.00 ^a	4.00±1.00 ^b	6.00±0.00 ^b
	3	3.00±0.00 ^a	4.00±0.00 ^c	3.00±0.00 ^a	4.00±0.00 ^a	5.00±0.00 ^a	6.00±0.00 ^a
SB	1	4.00±1.00 ^a	4.00±0.00 ^c	4.00±0.00 ^a	3.00±0.00 ^b	4.00±1.00 ^b	3.00±0.00 ^d
	2	4.00±1.00 ^a	6.00±0.00 ^a	4.00±0.00 ^a	3.00±0.00 ^b	4.00±0.00 ^b	5.00±0.00 ^b
	3	3.00±0.00 ^a	4.00±0.00 ^c	4.00±0.00 ^a	4.00±1.00 ^a	5.00±0.00 ^a	6.00±0.00 ^a
RB	1	3.00±1.00 ^a	3.00±0.00 ^d	ND	3.00±0.00 ^b	5.00±0.00 ^a	3.00±0.00 ^d
	2	4.00±1.00 ^a	4.00±1.00 ^c	ND	4.00±0.00 ^a	4.00±0.00 ^b	4.00±0.00 ^c
	3	4.00±1.00 ^a	5.00±0.00 ^b	4.00±0.00 ^a	4.00±0.00 ^a	4.00±0.00 ^b	5.00±0.00 ^b

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$. **Trts** – Treatments; **StB** – Standard Biochar; **SB** – Sorghum Biochar; **RB** - Rice Biochar; **ND**- Not determined

Table 8: Effects of different concentrations of biochars on leaf area (cm²) of *Zea mays* in 2018 and 2019

Trts	Rates (%)	2018			2019		
		Week 4	Week 5	Week 6	Week 4	Week 5	Week 6
Control	0	12.53±3.79 ^b	11.14±2.33 ^c	14.22±3.17 ^c	29.25±3.37 ^{ab}	36.07±6.67 ^c	56.21±17.97 ^{bc}
StB	1	9.43±2.09 ^c	17.80±2.62 ^{bc}	14.81±0.96 ^c	21.26±2.88 ^c	19.42±2.17 ^{ef}	20.00±5.87 ^d
	2	19.09±4.93 ^a	19.07±4.31 ^{abc}	23.33±11.7 ^{bc}	29.44±3.56 ^{ab}	52.23±4.83 ^a	66.93±19.53 ^{ab}
	3	12.45±3.75 ^b	15.61±0.64 ^{bc}	19.61±1.02 ^c	34.59±1.40 ^a	48.08±6.31 ^{ab}	62.95±17.33 ^{bc}
SB	1	17.23±5.24 ^a	19.13±4.89 ^{abc}	19.27±3.14 ^c	21.74±5.46 ^c	19.46±7.51 ^{ef}	17.52±0.81 ^d
	2	22.56±13.4 ^a	24.72±9.71 ^{ab}	33.32±16.03 ^b	26.49±1.63 ^{bc}	37.07±10.81 ^c	70.38±30.71 ^{ab}
	3	15.60±2.81 ^a	16.27±5.32 ^{bc}	18.11±1.63 ^c	26.17±3.31 ^{bc}	43.96±3.71 ^b	90.75±3.72 ^a
RB	1	9.08±2.76 ^c	14.50±2.06 ^{bc}	ND	27.20±0.69 ^{bc}	25.54±0.46 ^{de}	20.16±3.83 ^d
	2	14.89±15.5 ^b	24.72±12.58 ^{ab}	ND	29.04±4.71 ^{ab}	32.44±0.94 ^{cd}	29.37±7.22 ^d
	3	19.73±1.77 ^a	30.90±7.53 ^a	51.89±0.00 ^a	24.35±1.49 ^{bc}	27.55±2.85 ^d	36.70±1.49 ^{cd}

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$. **Trts** – Treatments; **StB** – Standard Biochar; **SB** – Sorghum Biochar; **RB** - Rice Biochar, **ND**- Not determined

Table 9: Effects of different concentrations of biochars on stem girth (cm) of *Zea mays* in 2018 and 2019

Trts	Rates (%)	2018	2019				
		Week 4	Week 5	Week 6	Week 4	Week 5	Week 6
Control	0	1.91±0.37 ^{ab}	2.19±0.15 ^c	2.29±0.09 ^e	1.93±0.09 ^b	2.67±0.27 ^{ab}	2.72±0.33 ^b
StB	1	2.09±0.23 ^{ab}	2.35±0.16 ^c	2.51±0.16 ^{de}	2.35±0.00 ^a	2.20±0.00 ^{cd}	1.88±0.00 ^c
	2	2.46±0.59 ^a	2.19±0.31 ^c	2.35±0.31 ^{de}	1.77±0.09 ^b	2.77±0.36 ^{ab}	2.66±0.00 ^b
	3	2.35±0.00 ^a	2.71±0.17 ^b	2.88±0.32 ^c	1.98±0.09 ^b	2.45±0.09 ^{bc}	1.88±0.00 ^c
SB	1	2.19±0.56 ^{ab}	2.50±0.31 ^{bc}	2.67±0.41 ^{cd}	1.88±0.00 ^b	2.67±1.00 ^{ab}	1.88±0.00 ^c
	2	2.13±0.49 ^{ab}	3.14±0.00 ^a	3.30±0.00 ^b	1.77±0.09 ^b	2.35±0.00 ^{bcd}	2.66±0.00 ^b
	3	2.14±0.09 ^{ab}	1.77±0.09 ^d	1.88±0.00 ^f	2.09±0.23 ^{ab}	2.51±0.54 ^{bc}	2.83±0.00 ^b
RB	1	1.56±0.14 ^b	2.24±0.09 ^c	ND	1.88±0.47 ^b	2.61±0.18 ^{abc}	1.82±0.09 ^c
	2	1.78±0.36 ^{ab}	3.29±0.15 ^a	ND	2.35±0.00 ^a	3.14±0.18 ^a	3.14±0.00 ^a
	3	1.57±0.00 ^b	3.14±0.00 ^a	6.60±0.00 ^a	1.88±0.00 ^b	1.94±0.08 ^d	1.93±0.19 ^c

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$. **Trts** – Treatments; **StB** – Standard Biochar; **SB** – Sorghum Biochar; **RB** - Rice Biochar, **ND**- Not determined

Table 10: Effects of different concentrations of biochars on height (cm) of *Pennisetum glaucum* in 2018 and 2019

Trts	Rates (%)	2018	2019				
		Week 4	Week 5	Week 6	Week 4	Week 5	Week 6
Control	0	10.23±3.29 ^d	20.55±3.45 ^e	28.33±2.58 ^{cd}	9.60±0.45 ^{bc}	11.27±1.70 ^d	13.26±1.13 ^{de}
StB	1	19.31±4.97 ^{abc}	23.37±3.84 ^{de}	27.10±5.05 ^{cd}	2.06±0.11 ^e	6.50±3.50 ^e	2.46±0.05 ^f
	2	14.77±1.49 ^{cd}	20.10±0.00 ^e	23.50±0.00 ^d	8.00±0.50 ^{cd}	15.70±1.80 ^{bc}	26.16±2.25 ^b
	3	16.72±4.06 ^{bcd}	19.90±1.40 ^e	35.60±0.00 ^{bc}	16.40±2.33 ^a	23.17±0.76 ^a	32.20±2.98 ^a
SB	1	17.61±2.96 ^{abc}	24.53±1.53 ^{cde}	ND	6.33±1.00 ^{cd}	7.16±0.28 ^e	7.96±0.89 ^{ef}
	2	22.47±3.86 ^{ab}	29.43±4.21 ^{bc}	34.17±1.50 ^{bc}	9.00±0.00 ^{bcd}	12.71±01.25 ^{cd}	20.86 ±1.95 ^{bc}
	3	22.91±3.66 ^{ab}	32.70±3.80 ^{ab}	42.85±9.45 ^{ab}	16.40±1.70 ^a	18.99±4.50 ^b	34.16±0.28 ^a
RB	1	24.57±4.45 ^a	35.47±4.96 ^a	43.47±1.08 ^{ab}	9.76±2.04 ^{bc}	10.35±0.56 ^{de}	14.30±1.41 ^d
	2	18.08±4.05 ^{abc}	27.35±0.95 ^{bcd}	35.93±4.20 ^{bc}	11.50±3.50 ^b	16.62±1.65 ^{bc}	24.76±3.80 ^{bc}
	3	24.10±2.52 ^a	35.97±4.31 ^a	49.87±6.53 ^a	10.93±0.66 ^{bc}	13.79±2.40 ^{cd}	20.00±8.50 ^c

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$. **Trts** – Treatments; **StB** – Standard Biochar; **SB** – Sorghum Biochar; **RB** - Rice Biochar, **ND**- Not determined

Table 11: Effects of different concentrations of biochars on leaf number of *Pennisetum glaucum* in 2018 and 2019

Trts	Rates (%)	2018			2019		
		Week 4	Week 5	Week 6	Week 4	Week 5	Week 6
Control	0	4.00±0.00 ^a	5.00±0.00 ^b	6.00±0.00 ^a	3.00±0.00 ^a	3.00±0.00 ^c	2.00±0.00 ^e
StB	1	4.00±0.00 ^a	4.00±0.00 ^c	4.00±0.00 ^c	3.00±0.00 ^a	3.00±0.00 ^c	3.33±0.00 ^{cd}
	2	4.00±0.00 ^a	4.00±0.00 ^c	6.00±0.00 ^a	3.00±0.00 ^a	4.00±0.00 ^b	5.00±0.00 ^b
	3	4.00±0.00 ^a	5.00±0.00 ^b	6.00±0.00 ^a	3.00±0.00 ^a	5.00±0.00 ^a	7.00±0.00 ^a
SB	1	4.00±0.00 ^a	5.00±0.00 ^b	ND	3.00±0.00 ^a	3.00±0.00 ^c	4.00±0.00 ^c
	2	3.00±0.00 ^b	5.00±0.00 ^b	4.00±0.00 ^c	3.00±0.00 ^a	4.00±0.00 ^b	5.00±0.00 ^b
	3	4.00±0.00 ^a	5.00±0.00 ^b	4.00±0.00 ^c	3.00±0.00 ^a	4.00±0.00 ^b	5.00±0.00 ^b
RB	1	3.00±0.00 ^b	6.00±0.00 ^a	6.00±0.00 ^a	3.00±0.00 ^a	3.00±0.00 ^c	3.00±0.00 ^d
	2	4.00±0.00 ^a	5.00±0.00 ^b	5.00±0.00 ^b	3.00±0.00 ^a	4.00±0.00 ^b	4.00±0.00 ^c
	3	4.00±0.00 ^a	5.00±0.00 ^b	5.00±0.00 ^b	3.00±0.00 ^a	4.00±0.00 ^b	5.00±0.00 ^b

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$. **Trts** – Treatments; **StB** – Standard Biochar; **SB** – Sorghum Biochar; **RB** - Rice Biochar; **ND**- Not determined

Table 12: Effects of different concentrations of biochars on leaf area (cm²) of *Pennisetum glaucum* in 2018 and 2019

Trts	Rates (%)	2018	2019				
		Week 4	Week 5	Week 6	Week 4	Week 5	Week 6
Control	0	2.27±1.00 ^b	5.44±1.58 ^{bc}	8.82±1.46 ^{cd}	0.54±0.62 ^c	2.06±0.24 ^b	1.89±0.32 ^b
StB	1	3.72±1.96 ^{ab}	3.98±0.69 ^{bc}	5.91±1.23 ^{cde}	0.40±0.10 ^c	0.26±0.12 ^d	0.15±0.00 ^d
	2	2.21±0.56 ^b	2.80±0.00 ^c	2.95±0.00 ^{de}	1.22±0.25 ^b	1.18±1.03 ^c	1.26±0.82 ^c
	3	3.35±1.21 ^{ab}	3.99±1.00 ^{bc}	8.88±0.00 ^{cd}	3.18±0.53 ^{ab}	1.47±0.82 ^c	1.28±0.20 ^c
SB	1	4.16±0.58 ^{ab}	5.03±2.41 ^{bc}	ND	0.68±0.18 ^c	0.68±0.20 ^d	0.75±0.17 ^c
	2	4.63±0.98 ^{ab}	5.99±1.41 ^{bc}	6.81±2.11 ^{cde}	1.47±0.01 ^b	1.79±0.51 ^{bc}	4.08±0.09 ^{ab}
	3	4.40±1.96 ^{ab}	8.08±0.14 ^{ab}	11.47±4.96 ^{bc}	4.55±0.42 ^a	3.51±1.63 ^a	5.90±2.05 ^a
RB	1	4.54±1.28 ^{ab}	10.08±2.20 ^a	17.27±8.68 ^{ab}	2.12±0.49 ^{ab}	1.28±0.01 ^c	1.84±0.02 ^b
	2	3.40±0.36 ^{ab}	3.95±0.59 ^{bc}	7.35±4.51 ^{cde}	2.07±0.52 ^{ab}	1.82±0.24 ^{bc}	4.64±0.60 ^{ab}
	3	5.41±1.92 ^a	11.36±5.71 ^a	20.41±7.69 ^a	1.55±0.04 ^b	2.27±0.73 ^b	5.92±8.49 ^a

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$. **Trts** – Treatments; **StB** – Standard Biochar; **SB** – Sorghum Biochar; **RB** - Rice Biochar; **ND**- Not determined; Unit - cm²

Table 13: Effects of different concentrations of biochars on stem girth (cm) of *Pennisetum glaucum* in 2018 and 2019

Trts	Rates (%)	2018			2019		
		Week 4	Week 5	Week 6	Week 4	Week 5	Week 6
Control	0	1.30±0.09 ^a	2.30±0.09 ^a	2.57±0.09 ^a	1.63±0.93 ^{ab}	1.04±0.08 ^{cd}	1.09±0.00 ^b
StB	1	0.94±0.00 ^b	1.57±0.00 ^c	1.71±0.00 ^c	0.67±0.35 ^b	0.72±0.32 ^e	0.47±0.00 ^c
	2	0.94±0.16 ^b	1.57±0.00 ^c	1.77±0.10 ^c	0.88±0.35 ^{ab}	0.62±0.00 ^e	1.98±0.46 ^a
	3	1.09±0.16 ^{ab}	1.57±0.00 ^c	1.77±0.09 ^c	1.14±0.08 ^{ab}	1.71±0.00 ^b	1.82±0.09 ^a
SB	1	1.09±0.16 ^{ab}	1.57±0.00 ^c	ND	0.77±0.40 ^{ab}	0.57±0.08 ^e	0.62±0.00 ^c
	2	1.09±0.16 ^{ab}	1.57±0.00 ^c	1.77±0.10 ^c	0.62±0.00 ^b	1.09±0.00 ^{cd}	1.66±0.08 ^a
	3	0.97±0.18 ^b	1.62±0.09 ^c	1.82±0.10 ^c	1.81±1.03 ^a	2.35±0.09 ^a	1.66±0.18 ^a
RB	1	1.09±0.16 ^{ab}	1.88±0.00 ^b	2.19±0.00 ^b	1.37±0.92 ^{ab}	0.84±0.08 ^{de}	1.09±0.00 ^b
	2	1.30±0.09 ^a	1.57±0.00 ^c	1.88±0.17 ^c	0.77±0.27 ^{ab}	1.09±0.00 ^{cd}	1.71±0.00 ^a
	3	1.30±0.24 ^a	1.67±0.18 ^c	1.93±0.24 ^c	1.09±0.00 ^{ab}	1.29±0.35 ^c	1.68±0.20 ^a

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$. **Trts** – Treatments; **StB** – Standard Biochar; **SB** – Sorghum Biochar; **RB** - Rice Biochar

The result of year 2018 showed that the stem girth of *Tithonia* raised on soil amended with 2% RB was significantly greater than those on the control soil throughout the experiment. Rice biochar (3%) amended soil produced *T. diversifolia* that had higher stem girth (Table 17). However, stem girth reduced with increase in the concentration of standard biochar while rice biochar had a steady increase. In 2019, 2% standard biochar significantly increased stem girth throughout the experiment. However, 3% SB produced *T. diversifolia* with the largest stem girth. The biochar amended soils produced *Tithonia* with higher stem girth than the control at the end of the experiment (Table 17).

In 2018, all biochar amended soil produced *Tithonia* except 3% StB with significantly ($p \leq 0.05$) higher leaf areas than control at week 4. Leaf area of *Tithonia* plant on the control soil at 6th week (2.45 cm^2) was significantly ($p \leq 0.05$) higher than those on the soils amended with all concentrations of standard and sorghum biochars (Table 16) but rice biochar effects were contrary. However, 1% RB produced *Tithonia* plant with the largest leaf area all through the experiment (Table 16). Increase in standard biochar concentrations reduced the leaf area of *T. diversifolia* while increase in sorghum biochar concentrations increased the leaf area of *Tithonia diversifolia*. All through the experiment in year 2019, 2% StB and 1% and 3% SB treatments significantly affected the leaf area positively when compared to control.

In the year 2018, leaf number of *Tithonia* produced on 1% and 3% RB amended soil, 8.00 and 7.00 respectively were significantly greater than the plants on untreated soils (Table 15). However, *T. diversifolia* raised on 1% RB amended soil had the highest number of leaves. Higher leaf number was recorded in *Tithonia* raised on the control soil than in those on the biochar amended soils in 2019 (Table 15).

In 2018, all concentrations of rice biochar applied produced *Tridax procumbens* that were significantly ($p \leq 0.05$) taller than the control throughout the experiment (Table 18). There was a very poor response to standard and sorghum biochar treatments by *T. procumbens*. However, *T. procumbens* raised on 3% RB amended soil produced the tallest plant all through the experiment. *Tridax* height increased with increase in rice biochar. In 2019, 3% SB significantly enhanced *Tridax* height throughout the experiment. In addition, there was a steady increase with increase in sorghum biochar treatment.

Table 20 reveals that rice biochar treatment significantly increased ($p \leq 0.05$) the leaf area when compared to the control of *T. procumbens* in 2018. Poor response of *T. procumbens* was observed in standard and sorghum-biochar treatments. However, 3% RB treatment produced the largest leaf area of *T. procumbens* all through the experiment. Increase in rice biochar treatment significantly resulted in increased leaf area. In the year 2019, all biochar treatments at 2% significantly had positive effects on the *Tridax* leaf area at week 4. At 5th and 6th week, control significantly produced larger leaf area than the biochar treatments.

In the year 2018, number of leaves of *T. procumbens* were significantly higher than the control at week 6 after being treated with rice biochar treatments (Table 19). Though, 3% RB showed highest number of leaves at weeks 4, 5 and 6. The result of year 2019 revealed that the number of leaves of *Tridax* raised on the control soils were significantly higher than those on the soils amended with 2% StB and 3% RB at week 5 and 6, respectively. Initially, RB treatment enhanced the growth of *Tridax* but at the end, the control had a better growth.

Table 14: Effect of different concentrations of biochars on height (cm) of *Tithonia diversifolia* in 2018 and 2019

Trts	Rates (%)	2018			2019		
		Week 4	Week 5	Week 6	Week 4	Week 5	Week 6
Control	0	6.27±0.38 ^{bcd}	7.20±0.70 ^c	9.60±0.95 ^{bcd}	5.60±0.90 ^b	5.50±1.50 ^{bc}	6.00±1.32 ^{bc}
StB	1	5.30±1.06 ^{cd}	7.63±1.42 ^{bc}	9.40±1.61 ^{bcd}	0.00±0.00 ^d	0.00±0.00 ^e	0.00±0.00 ^e
	2	4.77±0.25 ^{de}	5.57±0.31 ^d	8.27±0.72 ^d	9.00±1.00 ^a	5.76±4.14 ^{abc}	8.16±5.75 ^{ab}
	3	3.50±0.10 ^e	5.00±0.00 ^d	5.50±0.20 ^e	0.00±0.00 ^d	0.00±0.00 ^e	0.50±0.00 ^e
SB	1	6.73±1.56 ^{bc}	8.80±1.13 ^b	ND	5.66±2.51 ^b	7.50±1.50 ^{ab}	8.50±1.50 ^{ab}
	2	6.17±0.15 ^{bcd}	7.03±0.49 ^d	8.93±0.85 ^{cd}	5.00±1.73 ^b	6.90±3.35 ^{ab}	6.50±2.50 ^{bc}
	3	6.13±0.40 ^{bcd}	8.13±0.40 ^{bc}	10.33±0.25 ^{bc}	5.83±0.28 ^b	9.00±0.00 ^a	11.00±0.00 ^a
RB	1	7.13±0.40 ^b	8.43±0.23 ^{bc}	10.70±0.46 ^b	3.06±0.51 ^c	3.53±0.45 ^{cd}	7.93±3.50 ^{ab}
	2	8.67±0.21 ^a	10.53±0.06 ^a	12.90±0.72 ^a	1.50±0.00 ^{cd}	1.50±0.00 ^{de}	1.50±0.72 ^d
	3	9.07±1.79 ^a	11.10±1.51 ^a	13.37±1.08 ^a	2.00±0.00 ^c	2.50±0.00 ^{cde}	3.50±0.00 ^{cd}

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$. **Trts** – Treatments; **StB** – Standard Biochar; **SB** – Sorghum Biochar; **RB** - Rice Biochar

Table 15: Effects of different concentrations of biochars on the leaf number of *Tithonia diversifolia* in 2018 and 2019

Trts	Rates (%)	2018	2019				
		Week 4	Week 5	Week 6	Week 4	Week 5	Week 6
Control	0	5.00±0.00 ^b	5.00±0.00 ^c	6.00±0.00 ^c	4.00±0.00 ^b	6.00±0.00 ^b	8.00±0.00 ^a
StB	1	4.00±0.00 ^c	5.00±0.00 ^c	4.00±0.00 ^e	0.00±0.00 ^d	0.00±0.00 ^e	0.00±0.00 ^e
	2	4.00±0.00 ^c	6.00±0.00 ^b	6.00±0.00 ^c	5.00±1.00 ^a	6.00±2.00 ^b	5.00±4.58 ^b
	3	3.00±0.00 ^d	3.00±0.00 ^e	4.00±0.00 ^e	0.00±0.00 ^d	0.00±0.00 ^e	4.00±0.00 ^{bc}
SB	1	5.00±0.00 ^b	4.00±0.00 ^d	ND	4.00±0.00 ^b	5.00±1.00 ^{bc}	5.00±1.73 ^b
	2	5.00±0.00 ^b	5.00±0.00 ^c	4.00±0.00 ^e	5.00±1.00 ^a	4.00±0.00 ^{cd}	6.00±0.00 ^{ab}
	3	5.00±0.00 ^b	4.00±0.00 ^d	5.00±0.00 ^d	4.00±0.00 ^b	8.00±0.00 ^a	6.00±0.00 ^{ab}
RB	1	5.00±0.00 ^b	7.00±0.00 ^a	8.00±0.00 ^a	4.00±0.00 ^b	4.00±0.00 ^{cd}	4.00±0.00 ^{bc}
	2	6.00±0.00 ^a	6.00±0.00 ^b	6.00±0.00 ^c	2.00±0.00 ^c	3.00±0.00 ^d	2.00±0.00 ^{cd}
	3	5.00±0.00 ^b	5.00±0.00 ^c	7.00±0.00 ^b	4.00±0.00 ^b	4.00±0.00 ^{cd}	4.00±0.00 ^{bc}

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$. **Trts** – Treatments; **StB** – Standard Biochar; **SB** – Sorghum Biochar; **RB** - Rice Biochar

Table 16: Effects of different concentrations of biochars on the leaf area (cm²) of *Tithonia diversifolia* in 2018 and 2019

Trts	Rates (%)	2018			2019		
		Week 4	Week 5	Week 6	Week 4	Week 5	Week 6
Control	0	0.89±0.46 ^a	1.41±0.73 ^{ab}	2.45±1.75 ^{abc}	0.59±0.01 ^{ab}	0.77±0.11 ^{ab}	1.00±0.03 ^{bc}
StB	1	1.01±0.64 ^a	1.63±0.57 ^{ab}	1.70±0.32 ^{abc}	0.00±0.00 ^b	0.00±0.00 ^b	0.00±0.00 ^c
	2	0.95±0.01 ^a	1.13±0.17 ^{ab}	1.58±0.29 ^{abc}	1.37±1.56 ^a	2.81±3.44 ^a	7.77±6.37 ^a
	3	0.59±0.09 ^a	0.36±0.00 ^b	0.40±0.26 ^{bc}	0.00±0.00 ^b	0.00±0.00 ^b	0.52±0.00 ^c
SB	1	1.51±0.55 ^a	1.93±0.95 ^{ab}	ND	0.69±0.22 ^{ab}	1.11±0.35 ^{ab}	1.64 ±1.31 ^{bc}
	2	1.12±0.85 ^a	1.37±0.49 ^{ab}	1.06±0.26 ^{abc}	0.56±0.16 ^{ab}	1.11±0.56 ^{ab}	0.89±0.67 ^{bc}
	3	1.13±0.36 ^a	1.10±0.30 ^b	1.74±0.48 ^{abc}	1.02±0.51 ^{ab}	2.13±0.37 ^{ab}	4.61±0.60 ^{ab}
RB	1	1.40±0.24 ^a	2.17±0.44 ^{ab}	5.08±3.95 ^a	0.45±0.11 ^{ab}	0.51±0.10 ^b	0.60±0.14 ^c
	2	1.52±0.53 ^a	1.83±1.03 ^{ab}	3.42±2.59 ^{abc}	0.02±0.00 ^b	0.04±0.00 ^b	0.04±0.00 ^c
	3	1.73±1.32 ^a	3.61±3.59 ^a	4.40±4.25 ^{ab}	0.21±0.00 ^b	0.29±0.00 ^b	0.30±0.00 ^c

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$. **Trts** – Treatments; **StB** – Standard Biochar; **SB** – Sorghum Biochar; **RB** - Rice Biochar

Table 17: Effects of different concentrations of biochars on stem girth (cm) of *Tithonia diversifolia* in 2018 and 2019

Trts	Rates (%)	2018	2019				
		Week 4	Week 5	Week 6	Week 4	Week 5	Week 6
Control	0	0.78±0.00 ^{bc}	1.30±0.09 ^c	1.46±0.09 ^{cde}	1.30±0.09 ^a	1.38±0.00 ^{ab}	1.41±0.00 ^{cd}
StB	1	0.57±0.17 ^{cd}	1.41±0.00 ^{bc}	1.66±0.08 ^c	0.00±0.00 ^c	0.00±0.00 ^d	0.00±0.00 ^e
	2	0.52±0.09 ^{cd}	1.36±0.09 ^{bc}	1.62±0.08 ^{cd}	1.41±0.16 ^a	1.57±0.09 ^a	1.51±0.23 ^{cd}
	3	0.47±0.01 ^d	0.94±0.00 ^d	1.25±0.00 ^e	0.00±0.00 ^c	0.00±0.00 ^d	1.25±0.00 ^d
SB	1	0.72±0.08 ^{bcd}	1.36±0.18 ^{bc}	ND	1.41±0.27 ^a	1.57±0.00 ^a	1.51± 0.17 ^{cd}
	2	0.78±0.00 ^{bc}	1.20±0.09 ^{cd}	1.52±0.09 ^{cde}	1.30±0.18 ^a	1.33±0.00 ^{ab}	1.46±0.09 ^{cd}
	3	0.73±0.09 ^{bcd}	1.09±0.15 ^{cd}	1.33±0.09 ^{de}	1.25±0.16 ^{ab}	1.33±0.00 ^{ab}	2.19±0.00 ^a
RB	1	0.78±0.00 ^{bc}	1.25±0.00 ^{cd}	1.57±0.00 ^{cde}	1.09±0.00 ^{ab}	1.25±0.00 ^{bc}	1.67±0.47 ^{bc}
	2	0.94±0.00 ^{ab}	1.67±0.18 ^{ab}	1.98±0.18 ^b	0.95±0.00 ^b	0.98±0.00 ^c	1.57±0.00 ^{bcd}
	3	1.16±0.40 ^a	1.83±0.45 ^a	2.30±0.48 ^a	1.15±0.36 ^{ab}	1.33±0.00 ^{ab}	1.88±0.00 ^b

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$. **Trts** – Treatments; **StB** – Standard Biochar; **SB** – Sorghum Biochar; **RB** - Rice Biochar

Table 18: Effects of different concentrations of biochars on the height (cm) of *Tridax procumbens* in 2018 and 2019

Trts	Rates (%)	2018			2019		
		Week 4	Week 5	Week 6	Week 4	Week 5	Week 6
Control	0	0.60±0.00 ^c	1.00±0.20 ^{bc}	1.40±0.62 ^b	0.90±0.10 ^b	0.75±0.25 ^d	0.75±0.25 ^b
StB	1	ND	ND	ND	ND	ND	ND
	2	ND	ND	ND	0.90±0.00 ^b	0.95±0.05 ^c	0.75±0.25 ^b
	3	0.00±0.00 ^d	1.20±0.00 ^{abc}	0.50±0.00 ^c	ND	ND	ND
SB	1	1.10±0.20 ^b	1.10±0.10 ^{abc}	ND	ND	ND	ND
	2	0.00±0.00 ^d	0.60±0.10 ^{cd}	ND	0.50±0.00 ^c	0.50±0.00 ^e	1.25±0.25 ^a
	3	0.00±0.00 ^d	0.90±0.79 ^{bc}	ND	1.00±0.00 ^{ab}	1.25±0.25 ^b	1.30±0.00 ^a
RB	1	1.10±0.00 ^b	1.40±0.40 ^{ab}	1.67±0.15 ^b	ND	ND	ND
	2	1.53±0.38 ^a	1.67±0.35 ^a	1.77±0.25 ^b	1.06±0.15 ^a	1.50±0.00 ^a	0.50±0.00 ^b
	3	0.83±0.35 ^{bc}	1.67±0.41 ^a	2.33±0.61 ^a	0.00±0.00 ^d	0.00±0.00 ^f	0.50±0.00 ^b

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$. **Trts** – Treatments; **StB** – Standard Biochar; **SB** – Sorghum Biochar; **RB** - Rice Biochar

Table 19: Effects of different concentrations of biochars on the leaf number of *Tridax procumbens* in 2018 and 2019

Trts	Rates (%)	2018			2019		
		Week 4	Week 5	Week 6	Week 4	Week 5	Week 6
Control	0	2.00±0.00 ^b	2.00±0.00 ^b	2.00±0.00 ^b	2.00±0.00 ^a	4.00±0.00 ^a	4.00±0.00 ^a
StB	1	ND	ND	ND	ND	ND	ND
	2	ND	ND	ND	2.00±0.00 ^a	2.00±0.00 ^b	4.00±0.00 ^a
	3	0.00±0.00 ^c	2.00±0.00 ^b	2.00±0.00 ^b	ND	ND	ND
SB	1	2.00±0.00 ^b	4.00±0.00 ^a	ND	ND	ND	ND
	2	0.00±0.00 ^c	2.00±0.00 ^b	ND	2.00±0.00 ^a	4.00±0.00 ^a	4.00±0.00 ^a
	3	0.00±0.00 ^c	2.00±0.00 ^b	ND	2.00±0.00 ^a	4.00±0.00 ^a	4.00±0.00 ^a
RB	1	2.00±0.00 ^b	2.00±0.00 ^b	4.00±0.00 ^a	ND	ND	ND
	2	2.00±0.00 ^b	2.00±0.00 ^b	4.00±0.00 ^a	2.00±0.00 ^a	4.00±0.00 ^a	4.00±0.00 ^a
	3	4.00±0.00 ^a	4.00±0.00 ^a	4.00±0.00 ^a	0.00±0.00 ^b	0.00±0.00 ^c	2.00±0.00 ^b

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$. **Trts** – Treatments; **StB** – Standard Biochar; **SB** – Sorghum Biochar; **RB** - Rice Biochar

Table 20: Effect of different concentrations of biochars on the leaf area (cm²) of *Tridax procumbens* in 2018 and 2019

Trts	Rates (%)	2018			2019		
		Week 4	Week 5	Week 6	Week 4	Week 5	Week 6
Control	0	0.01±0.00 ^c	0.10±0.00 ^a	0.14±0.09 ^a	0.01±0.00 ^c	0.04±0.00 ^a	0.05±0.09 ^a
StB	1	ND	ND	ND	ND	ND	ND
	2	ND	ND	ND	0.03±0.00 ^a	0.03±0.01 ^b	0.02±0.01 ^c
	3	0.00±0.00 ^c	0.05±0.00 ^b	0.05±0.00 ^b ^c	ND	ND	ND
SB	1	0.03±0.00 ^b	0.09±0.00 ^{ab}	ND	ND	ND	ND
	2	0.00±0.00 ^c	0.05±0.00 ^b	ND	0.03±0.00 ^a	0.02±0.00 ^c	0.00±0.00 ^d
	3	0.00±0.00 ^c	0.09±0.00 ^{ab}	ND	0.01±0.00 ^c	0.02±0.00 ^c	0.03±0.01 ^b
RB	1	0.03±0.00 ^b	0.09±0.00 ^{ab}	0.08±0.02 ^b	ND	ND	ND
	2	0.04±0.01 ^a	0.11±0.02 ^a	0.09±0.00 ^b	0.02±0.01 ^b	0.02±0.00 ^c	0.03±0.01 ^b
	3	0.01±0.01 ^c	0.10±0.04 ^a	0.16±0.03 ^a	0.00±0.00 ^d	0.00±0.00 ^d	0.04±0.02 ^b

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$. **Trts** – Treatments; **StB** – Standard Biochar; **SB** – Sorghum Biochar; **RB** - Rice Biochar

4.4. Effect of biochar on plant biomass

Table 21 shows the effects of the biochars on the biomass of *Zea mays* in 2018 and 2019. It was observed in 2018 that the root length of *Zea mays* produced on soil treated with biochars had higher values than the control. The fresh and dry weight of the shoot of *Zea mays* produced on soil treated with biochars except 1% StB had higher values than those on the control soil. Moreover, fresh weight of the root of *Z. mays* grown on soil only treated with 1% SB had lower value when compared to those on the control soil. However, fresh weight of the root of *Z. mays* grown soil treated with 1% StB was statistically the same with those on the control soil. On the other hand, the control produced larger root dry weight than the dry weight of the root of *Zea mays* grown on soil treated with biochars except 1% and 3% StB and SB but statistically the same with those on the soil treated with 3% RB. The 3% RB produced the largest fresh root weight (0.61 ± 0.38 g/kg) while 1% StB produced the longest root length (23.77 ± 0.85 cm) in *Z. mays*. In all, the shoot fresh and dry weights were greater than the root fresh and dry weight.

In 2019, *Z. mays* grown on soil treated with biochars except 1% SB produced longer roots length than the control. Only the 3% StB, SB and RB and 2% RB produced larger shoot fresh weight, 2% SB produced larger root fresh weight while other treatments had the same root fresh weight statistically ($p \leq 0.05$). The 2% and 3% StB and SB and 2% RB had significantly ($p \leq 0.05$) higher shoot and root dry weight than the control while others had statistically the same dry weight. The 2% SB had the largest fresh root weight (6.52 ± 1.91 g/kg) while 3% StB produced the longest root length (64.36 ± 26.72 cm) of *Z. mays*. Increased standard biochar and sorghum biochar led to a steady increase in shoot fresh weight. Root length of *Zea mays* decreased with increase in standard biochar concentrations in 2018 but vice versa in year 2019.

Table 22 shows the effects of the biochars on the biomass of *Pennisetum glaucum* in 2018 and 2019. It was found that in 2018 that the root length and root dry weight of *Pennisetum glaucum* produced on soil treated with biochars had higher values than the control. On the other hand, the control produced larger shoot fresh weight than the treatments except 3% SB and 3% RB. *Pennisetum glaucum* grown on soils treated biochars produced larger root fresh weight than those on the control. In addition, *Pennisetum glaucum* grown on the soil treated with 1% StB and 2% SB were statistically the same with control. The soil treated with 1% and 2% StB and RB and 3% SB produced *Pennisetum glaucum* with larger shoot dry weight than the control soil. In all, the shoot fresh and dry weights were greater than the root fresh and dry weight. The increase in rice biochar treatments resulted in increased shoot fresh weight of *Pennisetum glaucum*.

In year 2019, *Pennisetum glaucum* grown on soil treated with 2% and 3% StB and SB and 1% RB produced longer root length of *Pennisetum glaucum* than those on the control soil. *Pennisetum glaucum* grown on soils treated with 2% and 3% StB and SB and 2% RB had larger shoot fresh weight than the control. Only 2% and 3% StB, 3% SB and all levels of RB significantly ($p \leq 0.05$) increased the root fresh weight of *P. glaucum* (Table 22). The 2% and 3% of all biochars had significantly ($p \leq 0.05$) greater shoot dry weight than the control. Root dry weight of *P. glaucum* on the control soil was statistically the same ($p \leq 0.05$) with those on soil treated with 1% StB and RB and 2% SB. Increased standard biochar and sorghum biochar increased the root length, shoot and root fresh weight of *Pennisetum glaucum*. Increased sorghum biochar concentration increased the shoot dry weight. *Pennisetum glaucum* grown on soil treated with 2% RB and 3% StB produced the longest root length (17.23 ± 9.29 cm) and (10.93 ± 2.17 cm) in 2018 and 2019, respectively (Table 22).

Table 23 shows the effects of the biochars on the biomass of *Tithonia diversifolia* in 2018 and 2019. It was observed in 2018 that the control soil produced longer root length in *Tithonia diversifolia* than the soils treated with biochars except for 2% SB and 1% and 2% RB. Only 1%, 2% and 3% RB produced larger shoot fresh weight than the control. *Tithonia* produced in soil treated with 1% StB, 2% SB and 1%, 2% and 3% RB had significantly ($p \leq 0.05$) larger root fresh weight than the control. The soil treated with 2% and 3% SB and 1%, 2% and 3% RB produced larger shoot dry weight of *Tithonia* than the control soil (Table 23). It was found that the control soil produced significantly ($p \leq 0.05$) larger root dry weight of *Tithonia* than the biochar treated soils except 2% SB. However, the control was statistically ($p \leq 0.05$) the same with the treatments.

In year 2019, only the 2% StB and 3% SB and RB treatments produced significantly ($p \leq 0.05$) longer root length of *Tithonia* than the control (Table 23). It was found that the shoot fresh weight of *Tithonia* produced on soil treated with 2% and 3% StB and all levels of SB had values greater than those produced on the control soil. The soils treated with 2% StB and 1%, 2% and 3% SB and 3% RB produced larger root fresh weight than the control soils. Moreover, only the 2% StB and 3% SB treated soils produced larger shoot dry weight of *Tithonia* than the control. The shoot dry weight of *Tithonia* produced on soil treated with 1% and 2% SB and 3% RB were statistically the same with those on the control soil ($p \leq 0.05$). The root dry weight of *Tithonia* grown on soil treated with 2% StB and 1%, 2% and 3% SB were statistically the same with those on the control soil ($p \leq 0.05$). In addition, from the result of 2019 experiment, increased concentrations of sorghum biochar resulted to steady increase in shoot fresh weight. Sorghum biochar at 2% and 3% had the longest root length (9.73 ± 2.46 cm) and (8.73 ± 1.66 cm) of *Tithonia diversifolia* in 2018 and 2019, respectively (Table 23).

Table 21: Effects of different concentrations of biochars on biomass of *Zea mays* in 2018 and 2019

Trts	Rates (%)	2018					2019				
		RL (cm)	SFW (g/kg)	RFW (g/kg)	SDW (g/kg)	RDW (g/kg)	RL (cm)	SFW (g/kg)	RFW (g/kg)	SDW (g/kg)	RDW (g/kg)
Control	0	13.93±7.52 ^b	0.98±0.33 ^{bc}	0.28±0.07 ^{bc}	0.14±0.01 ^{bc}	0.06±0.02 ^{ab}	16.76±7.58 ^{de}	1.96±0.97 ^{de}	2.25±2.38 ^b	0.44±0.21 ^{cdef}	0.21±0.06 ^b
StB	1	23.77±0.85 ^a	0.92±0.21 ^{bc}	0.28±0.05 ^{bc}	0.11±0.03 ^c	0.03±0.02 ^{cde}	34.00±6.34 ^{bcd}	0.82±0.41 ^e	1.75±0.16 ^b	0.30±0.02 ^{def}	0.43±0.13 ^{ab}
	2	22.47±4.72 ^{ab}	1.91±1.03 ^{ab}	0.41±0.22 ^{ab}	0.30±0.17 ^{ab}	0.05±0.01 ^{bcd}	41.26±5.58 ^{bc}	1.38±0.16 ^{de}	1.94±0.92 ^b	0.65±0.17 ^{bcd}	0.28±0.10 ^{ab}
	3	23.43±8.57 ^a	1.34±0.13 ^{abc}	0.29±0.14 ^{bc}	0.16±0.02 ^{bc}	0.03±0.03 ^{dde}	64.36±26.72 ^a	7.78±0.52 ^a	1.91±0.32 ^b	2.30±0.48 ^a	0.49±0.25 ^{ab}
SB	1	15.77±0.95 ^{ab}	1.61±0.27 ^{ab}	0.20±0.01 ^{bc}	0.15±0.04 ^{bc}	0.04±0.01 ^{bcd}	6.90±0.70 ^e	0.82±0.41 ^e	2.13±1.10 ^b	0.14±0.04 ^f	0.19±0.10 ^b
	2	14.63±5.62 ^{ab}	2.50±1.10 ^a	0.48±0.25 ^{ab}	0.36±0.09 ^a	0.09±0.03 ^a	37.43±6.06 ^{bcd}	1.38±0.16 ^{de}	6.52±1.91 ^a	0.75±0.13 ^{bc}	0.33±0.05 ^{ab}
	3	17.93±7.33 ^{ab}	1.28±0.43 ^{abc}	0.30±0.03 ^{bc}	0.17±0.09 ^{bc}	0.05±0.01 ^{bcd}	27.60±3.17 ^{cde}	7.78±0.52 ^a	1.33±0.35 ^b	0.66±0.34 ^{bcd}	0.31±0.34 ^{ab}
RB	1	0.00±0.00 ^c	0.00±0.00 ^d	0.00±0.00 ^d	0.00±0.00 ^d	0.00±0.00 ^f	19.90±9.59 ^{cde}	1.13±0.33 ^{de}	1.81±0.82 ^b	0.25±0.00 ^{ef}	0.27±0.05 ^{ab}
	2	0.00±0.00 ^c	0.00±0.00 ^d	0.00±0.00 ^d	0.00±0.00 ^d	0.00±0.00 ^f	51.30±10.35 ^{ab}	4.55±0.59 ^b	2.09±0.03 ^b	0.90±0.05 ^b	0.59±0.20 ^a
	3	19.27±1.35 ^{ab}	2.54±1.63 ^a	0.61±0.38 ^a	0.34±0.21 ^a	0.06±0.02 ^{ab}	28.73±15.40 ^{cd}	2.79±0.83 ^c	1.11±0.03 ^b	0.38±0.05 ^{def}	0.25±0.03 ^b

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$. **Trts** – Treatments; **StB** – Standard Biochar; **SB** – Sorghum Biochar; **RB** - Rice Biochar; **RL** – Root Length, **SFW** – shoot fresh weight; **RFW** – Root fresh weight; **SDW** – shoot dry weight; **RDW** – root dry weight

Table 22: Effect of different concentrations of biochars on biomass of *Pennisetum glaucum* in 2018 and 2019

Trts	Rates (%)	2018					2019				
		RL (cm)	SFW (g/kg)	RFW (g/kg)	SDW (g/kg)	RDW (g/kg)	RL (cm)	SFW (g/kg)	RFW (g/kg)	SDW (g/kg)	RDW (g/kg)
Control	0	6.97±0.85 ^{bc}	0.67±0.14 ^{bc}	0.06±0.01 ^{bc}	0.10±0.03 ^{bc}	0.001±0.00 ^c	6.53±0.55 ^{bcd}	0.07±0.03 ^{cd}	0.03±0.01 ^b	0.01±0.00 ^{bc}	0.00±0.00 ^c
StB	1	11.80±1.30 ^{ab}	0.28±0.13 ^{bc}	0.06±0.01 ^{bc}	0.11±0.05 ^{bc}	0.002±0.001 ^c	3.56±1.47 ^e	0.01±0.00 ^d	0.01±0.00 ^b	0.00±0.00 ^c	0.00±0.00 ^e
	2	15.90±5.80 ^a	0.13±0.15 ^c	0.09±0.01 ^{abc}	0.02±0.02 ^{cd}	0.002±0.001 ^c	7.30±1.60 ^{bc}	0.36±0.14 ^b	0.05±0.00 ^b	0.05±0.00 ^a	0.01±0.00 ^{abc}
	3	13.10±3.30 ^{ab}	0.38±0.19 ^{bc}	0.10±0.04 ^{ab}	0.11±0.05 ^{bc}	0.01±0.01 ^{bc}	10.93±2.17 ^a	0.63±0.21 ^a	0.06±0.01 ^b	0.03±0.02 ^{ab}	0.01±0.00 ^{abc}
SB	1	0.00±0.00 ^c	0.00±0.00 ^d	0.00±0.00 ^d	0.00±0.00 ^e	0.00±0.00 ^d	4.16± 0.28 ^{de}	0.02±0.00 ^d	0.02±0.00 ^b	0.01±0.00 ^{bc}	0.01± 0.00 ^{abc}
	2	9.93±1.11 ^{ab}	0.35±0.09 ^{bc}	0.06±0.04 ^{bc}	0.10±0.02 ^{bc}	0.01±0.02 ^{bc}	6.66±1.32 ^{bcd}	0.21±0.10 ^{bcd}	0.03±0.01 ^b	0.02±0.01 ^{bc}	0.00±0.00 ^c
	3	12.53±4.13 ^{ab}	1.12±0.87 ^{ab}	0.14±0.10 ^{ab}	0.14±0.05 ^b	0.05±0.02 ^a	8.23±1.25 ^b	0.26±0.20 ^{bc}	0.22±0.24 ^a	0.03±0.03 ^{ab}	0.02±0.01 ^a
RB	1	16.67±4.85 ^a	0.48±0.36 ^{bc}	0.12±0.03 ^{ab}	0.16±0.01 ^b	0.02±0.01 ^b	7.66±1.85 ^{bc}	0.07±0.01 ^{cd}	0.04±0.01 ^b	0.01±0.00 ^{bc}	0.00±0.00 ^c
	2	17.23±9.29 ^a	0.64±0.39 ^{bc}	0.09±0.06 ^{ab}	0.09±0.03 ^{bc}	0.01±0.01 ^{bc}	6.36±0.75 ^{bcd}	0.24±0.09 ^{bc}	0.07±0.03 ^b	0.05±0.02 ^a	0.02±0.01 ^a
	3	15.03±3.12 ^{ab}	1.88±1.07 ^a	0.15±0.07 ^a	0.24±0.12 ^a	0.03±0.02 ^b	5.00±1.80 ^{cde}	0.07±0.00 ^{cd}	0.07±0.01 ^b	0.02±0.00 ^{bc}	0.01±0.00 ^{abc}

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$. **Trts** – Treatments; **StB** – Standard Biochar; **SB** – Sorghum Biochar; **RB** - Rice Biochar; **RL** – Root Length, **SFW** – shoot fresh weight; **RFW** – Root fresh weight; **SDW** – shoot dry weight; **RDW** – root dry weight

Table 23: Effect of different concentrations of biochars on biomass of *Tithonia diversifolia* in 2018 and 2019

Trts	Rates (%)	2018					2019				
		RL (cm)	SFW (g/kg)	RFW (g/kg)	SDW (g/kg)	RDW (g/kg)	RL (cm)	SFW (g/kg)	RFW (g/kg)	SDW (g/kg)	RDW (g/kg)
Control	0	8.20±1.90 ^a	0.32±0.05 ^{abc}	0.06±0.02 ^{ab}	0.02±0.01 ^{bc}	0.02±0.03 ^a	5.50±5.63 ^{abc}	0.06±0.01 ^b	0.02±0.00 ^{cd}	0.01±0.00 ^c	0.01±0.00 ^a
StB	1	6.97±1.21 ^a	0.20±0.07 ^{bc}	0.10±0.02 ^a	0.02±0.01 ^{bc}	0.001±0.00 ^a	0.00±0.00 ^e	0.00±0.00 ^b	0.00±0.00 ^d	0.00±0.00 ^c	0.00±0.00 ^b
	2	5.50±0.40 ^a	0.20±0.01 ^{bc}	0.06±0.04 ^{ab}	0.01±0.001 ^c	0.002±0.001 ^a	6.40±1.80 ^{abc}	0.92±0.71 ^a	0.10±0.08 ^a	0.10±0.05 ^a	0.01±0.00 ^b
	3	8.17±0.55 ^a	0.09±0.01 ^{bc}	0.05±0.02 ^{ab}	0.002±0.001 ^c	0.001±0.001 ^a	3.10±0.00 ^{bcd}	0.08±0.00 ^b	0.00±0.00 ^d	0.00±0.00 ^c	0.00±0.00 ^b
SB	1	0.00±0.00 ^b	0.00±0.00 ^d	0.00±0.00 ^c	0.00±0.00 ^d	0.00±0.00 ^b	4.20±0.80 ^{bcd}	0.07±0.00 ^b	0.04±0.01 ^{bcd}	0.01±0.00 ^c	0.01±0.00 ^a
	2	9.73±2.46 ^a	0.17±0.04 ^{bc}	0.07±0.05 ^a	0.05±0.01 ^{abc}	0.02±0.03 ^a	3.23±0.75 ^{bcd}	0.11±0.07 ^b	0.08±0.04 ^{ab}	0.01±0.00 ^c	0.01±0.01 ^a
	3	6.23±0.45 ^a	0.25±0.07 ^{bc}	0.05±0.03 ^{ab}	0.12±0.08 ^a	0.001±0.001 ^a	8.73±1.66 ^a	0.28±0.09 ^b	0.06±0.01 ^{abc}	0.05±0.03 ^b	0.01±0.00 ^a
RB	1	8.40±6.02 ^a	0.47±0.31 ^{ab}	0.08±0.04 ^a	0.08±0.07 ^{abc}	0.01±0.01 ^a	2.90±1.35 ^{cde}	0.00±0.00 ^b	0.00±0.00 ^d	0.00±0.00 ^c	0.00±0.00 ^b
	2	8.83±1.17 ^a	0.47±0.15 ^{ab}	0.08±0.01 ^a	0.08±0.03 ^{abc}	0.001±0.001 ^a	1.40±0.00 ^{cd}	0.01±0.00 ^b	0.01±0.00 ^d	0.00±0.00 ^c	0.00±0.00 ^b
	3	8.00±2.54 ^a	0.65±0.55 ^a	0.07±0.06 ^a	0.09±0.08 ^{ab}	0.01±0.01 ^a	6.93±0.14 ^{ab}	0.05±0.01 ^b	0.03±0.01 ^{bcd}	0.01±0.00 ^c	0.00±0.00 ^b

Values are presented as means ± S.D of triplicate values. Values with different superscripts on the same column differ significantly at $p \leq 0.05$. **Trts** – Treatments; **StB** – Standard Biochar; **SB** – Sorghum Biochar; **RB** - Rice Biochar; **RL** – root length, **SFW** – shoot fresh weight; **RFW** – Root fresh weight; **SDW** – shoot dry weight; **RDW** – root dry weight

4.5 Biochar effect on heavy mobility in plants

Table 24 shows the effects of different biochars on the heavy metal contents of amended soils after planting of *Zea mays* in 2018 and 2019. In 2018, the Cu contents in the control soil was greater than the biochar amended soils except 3% SB and RB. All the biochar amended soils except 3% StB, 1% and 3% SB and 1% RB produced Zn contents that were statistically ($p \leq 0.05$) the same with the control soil. The Pb contents in the control soil was significantly ($p \leq 0.05$) greater than 2% StB and RB and 2% and 3% SB amended soils. Only 1% and 3% StB amended soils produced significantly ($p \leq 0.05$) greater Cd contents than the control soil. The Cr contents in all the biochar amended soils except 1% and 3% RB were significantly greater than the Cr contents in the control soil (Table 24).

In 2019, Cu content in the control soil was more than the Cu contents in 1%, 2% and 3% StB and 2% SB amended soils. Only 1% and 2% RB amended soils produced greater Zn contents than the control soil. The Pb content in 2% RB amended soil was significantly ($p \leq 0.05$) greater than the Pb contents in the control soil. However, the control soil produced greater Cd content than the biochars treated soils. The 1% SB and RB amended soils had significantly ($p \leq 0.05$) greater Cr contents than the control soil. Increased in the RB concentrations led to a steady decrease in the Cu contents (Table 24).

Table 25 shows the effects of different biochars on the heavy metal contents of the root of *Zea mays* in 2018 and 2019. It was observed that in 2018, Cu contents of the roots of *Z. mays* grown on soil amended with all the biochars except in 1% and 2% RB were lower than the control. The Zn contents of roots of *Z. mays* grown on soil amended with 1% and 2% StB and 3% SB were found to be statistically ($p \leq 0.05$) the same with the Zn content of the control (Table 25). The Pb

contents in the roots of *Z. mays* were found to be statistically ($p \leq 0.05$) the same but numerically greater. The Cd contents in the root of *Z. mays* grown on control soil was significantly ($p \leq 0.05$) greater than those on the biochar amended soils except 2% RB. The Cr contents were more in the roots of *Z. mays* in all treatments except for 3% StB, 2% SB and 1% RB.

In 2019, Cu, Zn and Cr content of root of *Z. mays* produced on control soil was more than those on biochar amended soils except 2% StB and RB and 1% and 3% SB. (Table 25). Furthermore, the Pb contents in *Z. mays* produced on the control soil were more than those on the biochar amended soils while only 3% SB treatment had more Cd contents than the control (Table 25).

Table 26 shows the effects of different biochars on the heavy metal contents of the shoot of *Zea mays* in 2018 and 2019. In 2018, Cu contents in shoot of *Z. mays* raised on soils treated with 2% and 3% RB were found to be statistically ($p \leq 0.05$) the same with the control. The Zn contents in the shoots of *Z. mays* produced on amended soils were more than the control. The Pb contents in the shoots of *Z. mays* grown on soils amended with all the biochars except 3% RB were found to be statistically ($p \leq 0.05$) the same with the control. The Cd contents in the shoot of *Z. mays* grown on control soil was greater than those grown on soil amended with all biochars except 1% StB and 2% RB. The Cr contents in the shoot of *Z. mays* raised on the control soil was found to be more than those grown on soil treated biochars except 1% StB and 3% RB (Table 26). In 2019, the Cu contents in the shoot of *Z. mays* grown on control soil was more than those grown on the soils amended with 1% and 2% StB and 1% and 3% RB. *Zea mays* produced on soil treated with all the biochars except 2% StB had greater Zn contents in their shoot than those on the control soil. However, Pb contents in shoot of *Z. mays* raised on soils amended with 2% StB and RB were statistically ($p \leq 0.05$) the same with those on the control soil. Soils amended with 1% and 2% StB and 1% and 3% RB produced lower content of Cr in the shoot of *Z. mays* when

compared to the control soil. Only Pb and Zn contents were found to be less than the permissible limit. With respect to the interaction of biochar and percentage rate, there was a significant effect on the heavy metal concentrations of *Zea mays* in both years (Table 26).

Table 27 shows the effects of different biochars on the heavy metal contents of amended soil after planting of *Pennisetum glaucum* in 2018 and 2019. In 2018, the Cu contents in all the biochar amended soils except 3% STB and RB and 2% SB were greater than the Cu contents in the control soil. The control soil significantly ($p \leq 0.05$) produced Zn content greater than the Zn contents in the biochar amended soils except 2% StB and 1% and 3% SB amended soils. The Pb contents in 2% StB and 1% SB amended soils were greater than the Pb content in the control soil. Also, 3% STB and 1% SB amended soils produced significantly ($p \leq 0.05$) Cd contents greater than the control soil. All the biochar amended soils except 1% and 2% RB significantly ($p \leq 0.05$) produced greater Cr contents than the control soil (Table 27). Increase in rice biochar concentrations decreased the Cu content. In addition, increase in the levels of sorghum biochar resulted to a decrease in Pb, Cd and Cr contents. In 2019, the control soil produced Cu content greater than 3% StB and 2% RB amended soils but statistically the same with 3% SB amended soil ($p \leq 0.05$). The Zn contents in 1% StB, 1% and 2% SB and 1% and 3% RB amended soils were higher than the Zn content in the control soil. The Pb contents in 1% StB, 1% and 2% SB and 1% RB amended soils were significantly ($p \leq 0.05$) greater than the Pb contents in the control soil. The control soil produced statistically ($p \leq 0.05$) the same Cd contents with 1% StB and RB amended but significantly ($p \leq 0.05$) lower than 2% SB amended soil. The biochar amended soils except 3% StB, 1% and 3% SB and 2% RB produced Cr contents greater than the control soil (Table 27).

Table 28 shows the effects of different biochars on the heavy metal contents of the root of *Pennisetum glaucum* in 2018 and 2019. It was observed that in 2018, the Cu and Pb contents in the root of *P. glaucum* grown on control soil were more than the biochar treatments except for 1% SB while only 1% StB had more Cd contents than the control. Furthermore, roots of *P. glaucum* grown on soils amended with 3% StB and 1% SB concentration had more Zn contents than the control. The Cr contents in the root of *P. glaucum* grown in the control soil were found to be statistically the same with Cr contents of *P. glaucum* on the 1% SB and 1% and 3% RB amended soil. The Cu, Zn and Pb contents in the roots of *P. glaucum* decreased with increase in sorghum biochar (Table 28). In 2019, it was observed that Cu, Zn, Pb and Cr contents in the root of *P. glaucum* of the control were more than the root of *P. glaucum* raised on soil amended with biochars while Cd contents in the root of *P. glaucum* amended with all the biochars were found to be statistically ($p \leq 0.05$) the same with the control. Moreover, increase in rice biochar increased the Cu contents in root of *P. glaucum*. The interaction of biochar and percentage rate had a significant effect on the heavy metal concentrations of *P. glaucum* in both years (Table 28).

Table 29 shows the effects of different biochars on the heavy metal contents of the shoot of *Pennisetum glaucum* in 2018 and 2019. In 2018, it was found that Cu contents in the shoots of *P. glaucum* of the control were more than the Cu contents in the shoots amended with biochars except 2% StB and % RB while only 1% RB had more Zn content than the control. The Pb contents of the *P. glaucum* grown on the control soil were found to be statistically ($p \leq 0.05$) the same with the shoots of *P. glaucum* on the biochar amended soils except for 2% StB and 3% RB. The biochar amended soils increased the amount of Cd contents in the shoots except in 2% and 3% RB when compared to the control soil. The Cr contents in the *P. glaucum* shoot raised on

soils amended with 2% StB and 1% and 3% RB were more than the Cr contents of the control (Table 29).

In 2019, it was observed that the Cu contents in the shoot of *P. glaucum* on soil amended with 1% StB and 2% SB were found to be significantly ($p \leq 0.05$) higher than those on the control. The Zn contents of the shoot of *P. glaucum* on the control soil were statistically ($p \leq 0.05$) the same with the Zn contents in the shoot raised on soils amended with 1% StB, 2% and 3% SB while the Pb contents of the shoot of *P. glaucum* on control soil were statistically ($p \leq 0.05$) the same with those on soils amended with 1% StB, 2% SB and 2% RB. However, Cd contents of the shoot of *P. glaucum* grown on soils amended with 1% StB, 2% SB and 2% RB were significantly ($p \leq 0.05$) higher than those on the control soil. Furthermore, Cr contents of the shoot of *P. glaucum* grown on control soil were statistically ($p \leq 0.05$) the same with those on soil amended with 1% StB, 2% and 3% SB and 1% RB. Only Pb contents were found to be lower than the permissible limit. The interaction of biochar and percentage rate had a significant effect on the heavy metal concentrations of *P. glaucum* in both years (Table 29).

Table 30 shows the effects of different biochars on the heavy metal contents in soil after planting of *Tithonia diversifolia* in 2018 and 2019. In 2018, the biochar amended soils except 2% StB and SB produced Cu contents greater than the control soil. The Zn contents in the control soil was statistically ($p \leq 0.05$) the same with the biochar amended soils except for 2% SB and 1% RB. The Pb contents in soil treated biochars except 2% and 3% SB were more than the Pb contents in the control soil. However, 1% and 2% StB treated soil had statistically ($p \leq 0.05$) the same Pb contents with the control soil. The Cd contents in the control soil was statistically ($p \leq 0.05$) the same with Cd contents in 2% and 3% SB and 3% RB treated soil. All the biochar amended soils except 1% StB produced higher Cr contents than the control soil (Table 30).

In 2019, the Cu contents in the biochar amended soils except 1% StB and 1% and 3% RB were more than the control soil. The Zn contents in 2% StB and 3% SB amended soil were significantly ($p \leq 0.05$) greater than the Zn content in the control soil. Only 2% SB amended soil produced significantly Pb and Cd contents higher than Pb and Cd contents in the control soil. The 1% StB and 1%, 2% and 3% RB amended soils produced Cr contents more than Cr contents in the soil (Table 30).

Table 31 shows the effects of different biochars on the heavy metal contents of the roots of *Tithonia diversifolia* in 2018 and 2019. It was found that in 2018, the biochar application increased the Cu contents in the roots of *T. diversifolia* raised on soils amended with all the biochars except 3% StB and 1% RB amended soils. The Zn and Cd contents of control were found to be statistically ($p \leq 0.05$) the same with Zn and Cd contents in the roots of *T. diversifolia* grown on soil amended with 3% StB, 1% and 2% SB. The Pb contents in the roots of *T. diversifolia* raised on soils amended with 2% StB, 1% RB and 3% RB were more than the Pb contents in the control soil. The Cr contents of the roots of *Tithonia* grown on soils amended with the biochars except 1% StB and 2% SB were more than the Cr contents of the root of *Tithonia* on control soil (Table 31).

In year 2019, the Cu contents in the *Tithonia* root on soils amended with the biochars increased except for 1% StB, 3% SB and 1% RB. Only 2% SB had more Zn and Pb contents than the control while Cd content in the root of *Tithonia* on soils amended with 2% SB and 3% RB were more than the control soil. The Cr contents of *Tithonia* root on the control soil was found to be statistically ($p \leq 0.05$) the same with the Cr contents in the root of *Tithonia* on soil amended biochars except for 2% StB, 1% and 2% SB and 3% RB (Table 31).

Table 32 shows the effects of different biochars on the heavy metal contents of the shoots of *Tithonia diversifolia* in 2018 and 2019. In 2018, the Cu contents in the *Tithonia* shoot of *T. diversifolia* on soils amended with all biochars were reduced except for 3% StB while the Zn contents were more in the shoot of *T. diversifolia* on soils amended with all biochars except for 1% and 2% StB and 3% RB. Furthermore, Pb contents of the control were more than the Pb contents in the treatments while 3% SB, 1% and 2% RB had more Cd contents than the control. Furthermore, the Cr contents in the shoot of *T. diversifolia* on soils amended with 2% and 3% StB and 3% SB were more than the Cr contents on the control soil. Increased concentrations of sorghum biochar increased the Cu contents in *T. diversifolia* shoot (Table 32).

In 2019, the Cu contents in the *Tithonia* shoots on soil amended with 2% StB was found to be significantly ($p \leq 0.05$) higher than the control. The Zn contents of *Tithonia* shoots on the control soil were found to be statistically ($p \leq 0.05$) the same with Zn contents of *Tithonia* on soil amended with 2% SB while the Pb contents of the control were statistically ($p \leq 0.05$) the same with the *Tithonia* shoots grown on biochar amended soils but numerically different from 2% SB. In addition, only 2% SB had more Cd contents in the shoot than the control while Cr content in the shoot of *Tithonia* on soils amended with 2% StB were significantly ($p \leq 0.05$) higher than the control. Only Pb was found to be less than the permissible limit. Biochar and percentage rate interaction had a significant effect on all the heavy metals concentration except Pb in 2018 (Table 32).

Table 33 shows the effects of different biochars on the heavy metal contents in soil after planting of *Tridax procumbens* in 2018 and 2019. In 2018, all the biochar amended soils except 3% StB and 1% SB had Cu content more than the control soil. The content of Zn in all the biochar amended soils except 3% StB were greater than Zn content in the control soil. The control soil

produced statistically ($p \leq 0.05$) the same Pb contents with 1%, 2% and 3% StB and 1% and 2% SB amended soil. However, the control soil produced statistically ($p \leq 0.05$) the same Cd contents with 1% and 2% StB and 2% and 3% SB amended soil. Furthermore, all the biochar treated soils except 2% and 3% StB and 3% SB had Cr contents more than the Cr content in the control soil (Table 33).

In 2019, the Cu content in the control soil was significantly ($p \leq 0.05$) greater than the Cu contents in the biochar amended soils except in 3% RB amended soil. The 2% and 3% RB amended soil had Zn contents greater than Zn content in the control soil. The Pb and Cd contents in the control soils were significantly ($p \leq 0.05$) greater than Pb and Cd contents in the biochar amended soils. The control soil had Cr content more than the Cr contents in the biochar amended soils except in 3% RB amended soil (Table 33).

Table 34 shows the effects of different biochars on the heavy metal contents of the roots of *Tridax procumbens* in 2018 and 2019. It was observed in 2018 that Cu contents in the roots of *T. procumbens* on soils amended with 2% RB was significantly ($p \leq 0.05$) higher than the Cu content of the control. The Zn contents in the roots of *T. procumbens* on soils amended with 1% RB and 3% RB were more than the control. The Pb contents of the control were statistically ($p \leq 0.05$) the same with Pb contents in the root of *T. procumbens* on soil amended with 1% RB while Cr contents of the control was statistically ($p \leq 0.05$) the same with 2% RB. The Cd content of the control was found to be significantly ($p \leq 0.05$) higher than the Cd contents in *T. procumbens* on all the amended soils. In year 2019, only 3% RB had more Cu and Cd contents in the *Tridax* roots than the control. The Zn, Pb and Cr contents of the control were found to be statistically ($p \leq 0.05$) the same with all the treatments (Table 34).

Table 35 shows the effects of different biochars on the heavy metal contents of the shoots of *Tridax procumbens* in 2018 and 2019. In 2018, only 1% RB had more Cu, Cd and Cr contents than the control in the shoot of *Tridax* while the Zn and Pb contents of the control were more than all the treatments. Zn increased in shoot with increase in rice biochar concentrations while Cu decreased with increase in rice biochar treatments (Table 35).

In 2019, only 3% RB had more Cu contents in the *Tridax* shoot than the control while Zn, Pb and Cd contents in the shoots of the control were statistically ($p \leq 0.05$) the same with all the treatments. The Cr contents of the control was significantly ($p \leq 0.05$) higher than the Cr content in the shoot amended with all the biochars. In addition, Zn and Pb were lower than the permissible limit. In 2019, all heavy metals investigated had lower concentrations than the permissible limit except for Cr in the shoot of *T. procumbens* on the control soil (5.00 mg/kg) and Cd in the root of *T. procumbens* on soil amended with 3% RB (2.33 mg/kg). Biochar and percentage rate interaction had a significant effect on the heavy metals except Cd in 2018.

Table 24: Effect of different concentrations of biochars on heavy metal content of soil after planting *Zea mays* in 2018 and 2019

Trts	Rate (%)	2018					2019				
		Cu	Zn	Pb	Cd	Cr	Cu	Zn	Pb	Cd	Cr
Control	0	0.66±0.57 ^f	0.16±0.05 ^{ab}	0.13±0.05 ^{bc}	0.16±0.05 ^b	1.33±0.57 ^d	21.33±1.15 ^c	0.00±0.00 ^c	0.00±0.00 ^b	2.33±0.57 ^a	2.00±0.00 ^b
StB	1	10.00±2.00 ^{be}	0.16±0.05 ^{ab}	0.20±0.00 ^{ab}	0.26±0.05 ^a	3.33±0.57 ^{bc}	11.33±1.15 ^e	0.00±0.00 ^c	0.00±0.00 ^b	0.00±0.00 ^c	1.00±0.00 ^c
	2	9.00±1.00 ^{ed}	0.13±0.05 ^{ab}	0.13±0.05 ^{bc}	0.13±0.05 ^b	3.33±0.57 ^{bc}	0.00±0.00 ^f	0.00±0.00 ^c	0.00±0.00 ^b	0.00±0.00 ^c	0.00±0.00 ^d
	3	12.66±1.15 ^a	0.23±0.05 ^a	0.26±0.05 ^a	0.26±0.05 ^a	4.66±0.57 ^a	12.00±0.00 ^e	0.00±0.00 ^c	0.00±0.00 ^b	0.00±0.00 ^c	1.00±0.00 ^c
SB	1	6.66±1.15 ^e	0.10±0.10 ^{bc}	0.13±0.05 ^{bc}	0.13±0.05 ^b	3.66±0.57 ^b	28.00±0.00 ^a	0.00±0.00 ^c	0.00±0.00 ^b	0.00±0.00 ^c	2.66±0.57 ^a
	2	10.00±1.00 ^{bc}	0.13±0.05 ^{ab}	0.10±0.05 ^c	0.00±0.00 ^c	1.66±0.57 ^d	0.00±0.00 ^f	0.00±0.00 ^c	0.00±0.00 ^b	0.00±0.00 ^c	0.00±0.00 ^d
	3	0.00±0.00 ^f	0.00±0.00 ^c	0.00±0.00 ^d	0.00±0.00 ^c	0.00±0.00 ^e	20.00±0.00 ^d	0.00±0.00 ^c	0.00±0.00 ^b	0.00±0.00 ^c	2.00±0.00 ^b
RB	1	7.33±1.15 ^{de}	0.10±0.00 ^{bc}	0.16±0.05 ^{bc}	0.13±0.05 ^b	0.00±0.00 ^e	24.33±0.57 ^b	4.00±0.00 ^a	0.00±0.00 ^b	1.00±0.00 ^b	2.66±0.57 ^a
	2	11.00±1.00 ^{ab}	0.13±0.05 ^{ab}	0.10±0.05 ^c	0.00±0.00 ^c	2.66±0.57 ^c	22.00±0.00 ^c	1.00±0.00 ^b	1.00±0.00 ^a	0.00±0.00 ^c	2.00±0.00 ^b
	3	0.00±0.00 ^f	0.13±0.05 ^{ab}	0.13±0.05 ^{bc}	0.13±0.05 ^b	1.66±0.57 ^d	20.00±0.00 ^d	0.00±0.00 ^c	0.00±0.00 ^b	0.00±0.00 ^c	2.00±0.00 ^b
PL		10.00	0.60	2.00	0.02	1.30	10.00	0.60	2.00	0.02	1.30
Sources of variation		Level of significance									
Biochar* Percentage		*	*	*	*	*	*	*	*	*	*

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$ (DMRT). **PL** –Permissible Limit (Source: World Health Organisation, 1996). Unit in mg/kg. **StB** – Standard Biochar, **SB** – Sorghum Biochar, **RB** –Rice Biochar, **TRTs** – Treatments

Table 25: Effect of different concentrations of biochars on heavy metal content in root of *Zea mays* in 2018 and 2019

Trts	Rates (%)	2018					2019				
		Cu	Zn	Pb	Cd	Cr	Cu	Zn	Pb	Cd	Cr
Control	0	8.00±1.73 ^{bc}	0.10±0.00 ^{abc}	0.06±0.05 ^{ab}	0.16±0.05 ^{ab}	0.00±0.00 ^d	33.33±1.15 ^e	6.33±0.57 ^c	1.00±0.00 ^a	1.00±0.00 ^b	4.00±0.00 ^d
StB	1	3.33±1.15 ^d	0.06±0.05 ^{abc}	0.13±0.05 ^a	0.13±0.05 ^{ab}	3.00±0.00 ^a	20.00±0.00 ^g	1.00±0.00 ^g	0.00±0.00 ^c	0.00±0.00 ^c	2.00±0.00 ^e
	2	1.66±0.57 ^{de}	0.10±0.10 ^{abc}	0.06±0.05 ^{ab}	0.13±0.05 ^{ab}	1.66±0.57 ^b	38.00±0.00 ^c	8.66±0.57 ^a	0.66±0.57 ^b	1.00±0.00 ^b	5.00±0.00 ^c
	3	7.00±1.00 ^c	0.13±0.05 ^{ab}	0.00±0.00 ^b	0.10±0.00 ^b	0.00±0.00 ^d	31.33±1.15 ^f	4.00±0.00 ^d	0.00±0.00 ^c	0.00±0.00 ^c	4.00±0.00 ^d
SB	1	1.66±0.57 ^{de}	0.03±0.05 ^{bc}	0.06±0.05 ^{ab}	0.10±0.00 ^b	1.00±0.00 ^c	46.00±0.00 ^b	7.00±0.00 ^b	0.00±0.00 ^c	0.10±0.00 ^c	6.00±0.00 ^b
	2	0.00±0.00 ^e	0.00±0.00 ^c	0.06±0.05 ^{ab}	0.00±0.00 ^c	0.00±0.00 ^d	32.66±2.30 ^{ef}	3.00±0.00 ^e	0.00±0.00 ^c	0.00±0.00 ^c	4.00±0.00 ^d
	3	6.66±1.15 ^c	0.10±0.00 ^{abc}	0.10±0.00 ^a	0.13±0.05 ^{ab}	2.66±0.57 ^a	55.33±1.15 ^a	9.00±0.00 ^a	0.00±0.00 ^c	2.33±0.57 ^a	8.00±0.00 ^a
RB	1	14.33±1.15 ^a	0.16±0.05 ^a	0.06±0.05 ^{ab}	0.13±0.05 ^{ab}	0.00±0.00 ^d	10.00±0.00 ^h	0.00±0.00 ^h	0.00±0.00 ^c	0.00±0.00 ^c	0.00±0.00 ^f
	2	9.33±2.30 ^b	0.16±0.05 ^a	0.13±0.05 ^a	0.20±0.00 ^a	2.33±0.57 ^a	35.33±1.15 ^d	7.00±0.00 ^b	0.00±0.00 ^c	0.00±0.00 ^c	4.00±0.00 ^d
	3	0.20±0.00 ^e	0.16±0.05 ^a	0.10±0.00 ^a	0.10±0.00 ^b	2.33±0.57 ^a	31.33±1.15 ^g	2.00±0.00 ^f	0.00±0.00 ^c	0.00±0.00 ^c	2.00±0.00 ^e
PL		10.00	0.60	2.00	0.02	1.30	10.00	0.60	2.00	0.02	1.30
Sources of variation		Level of significance									
Biochar* Percentage		*	*	*	*	*	*	*	*	*	*

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$ (DMRT). **PL** –Permissible Limit (Source: World Health Organisation, 1996). Unit in mg/kg. **StB** – Standard Biochar, **SB** – Sorghum Biochar, **RB** –Rice Biochar, **Trts** – Treatments

Table 26: Effect of different concentrations of biochars on heavy metal content in shoot of *Zea mays* in 2018 and 2019

Trts	Rates (%)	2018					2019				
		Cu	Zn	Pb	Cd	Cr	Cu	Zn	Pb	Cd	Cr
Ctrl	0	12.0±3.46 ^a	0.00±0.00 ^d	0.13±0.05 ^b	0.13±0.05 ^{bcd}	3.33±0.57 ^{ab}	28.00±0.00 ^f	0.33±0.57 ^h	0.00±0.00 ^d	1.00±0.00 ^d	3.00±0.00 ^f
StB	1	7.33±1.15 ^b	0.06±0.05 ^{bcd}	0.10±0.00 ^b	0.06±0.05 ^{de}	3.66±0.57 ^a	26.00±0.00 ^g	16.00±0.00 ^d	1.00±0.00 ^c	0.00±0.00 ^e	2.66±0.57 ^{fg}
	2	5.33±1.15 ^b	0.06±0.05 ^{bcd}	0.10±0.00 ^b	0.10±0.00 ^{cd}	2.66±0.57 ^{ab}	10.00±0.00 ^j	0.00±0.00 ^h	0.00±0.00 ^d	0.00±0.00 ^e	1.00±0.00 ⁱ
	3	7.66±1.52 ^b	0.10±0.10 ^{abcd}	0.13±0.05 ^b	0.20±0.00 ^{ab}	2.33±0.57 ^{bc}	32.00±0.00 ^e	6.66±0.57 ^f	1.00±0.00 ^c	1.00±0.00 ^d	4.00±0.00 ^e
SB	1	0.00±0.00 ^c	0.20±0.00 ^a	0.06±0.05 ^b	0.10±0.00 ^{cd}	1.33±0.57 ^c	69.33±1.15 ^b	11.33±0.57 ^e	1.00±0.00 ^c	2.00±0.00 ^c	10.00±0.00 ^b
	2	6.66±1.15 ^b	0.06±0.05 ^{bcd}	0.13±0.05 ^b	0.16±0.05 ^{bc}	2.66±0.57 ^{ab}	66.66±1.15 ^c	17.33±0.57 ^c	2.33±0.57 ^a	1.00±0.00 ^d	9.00±0.00 ^c
	3	1.66±0.57 ^c	0.03±0.05 ^{cd}	0.06±0.05 ^b	0.16±0.05 ^{bc}	3.00±0.00 ^{ab}	115.0±0.00 ^a	26.00±0.00 ^a	2.00±0.00 ^b	3.00±0.00 ^a	18.00±0.00 ^a
RB	1	0.00±0.00 ^c	0.16±0.05 ^{ab}	0.06±0.05 ^b	0.10±0.00 ^{cd}	0.00±0.00 ^d	18.00±0.00 ⁱ	1.00±0.00 ^g	1.00±0.00 ^c	0.00±0.00 ^e	2.00±0.00 ^h
	2	12.00±1.00 ^a	0.13±0.05 ^{abc}	0.03±0.05 ^b	0.00±0.00 ^e	2.66±1.15 ^{ab}	51.33±1.15 ^d	18.00±0.00 ^b	0.00±0.00 ^d	2.33±0.57 ^b	6.66±0.57 ^d
	3	14.00±2.00 ^a	0.10±0.00 ^{abcd}	0.23±0.05 ^a	0.26±0.05 ^a	3.33±0.57 ^{ab}	24.00±0.00 ^h	7.00±0.00 ^f	1.00±0.00 ^c	0.00±0.00 ^e	2.33±0.57 ^{gh}
PL		10.00	0.60	2.00	0.02	1.30	10.00	0.60	2.00	0.02	1.30
Sources of variation		Level of significance									
Biochar* Percentage		*	*	*	*	*	*	*	*	*	*

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$ (DMRT). **PL** –Permissible Limit (Source: World Health Organisation, 1996). Unit in mg/kg. **StB** – Standard Biochar, **SB** – Sorghum Biochar, **RB** –Rice Biochar, **Trts** – Treatments

Table 27: Effect of different concentrations of biochars on heavy metal content of soil after planting *Pennisetum glaucum* in 2018 and 2019

Trts	Rate (%)	2018					2019				
		Cu	Zn	Pb	Cd	Cr	Cu	Zn	Pb	Cd	Cr
Control	0	2.00±0.00 ^e	0.13±0.05 ^{bc}	0.13±0.05 ^{abc}	0.13±0.05 ^b	1.33±1.15 ^c	16.00±0.00 ^d	0.00±0.00 ^e	0.00±0.00 ^b	1.00±0.00 ^b	1.66±0.57 ^{cd}
StB	1	5.33±8.00 ^d	0.00±0.00 ^d	0.13±0.05 ^{abc}	0.10±0.00 ^b	2.66±0.57 ^a	20.00±0.00 ^e	7.00±0.00 ^b	1.00±0.00 ^a	1.00±0.00 ^b	2.00±0.00 ^c
	2	8.00±2.00 ^c	0.16±0.05 ^b	0.20±0.00 ^{ab}	0.13±0.05 ^b	1.66±0.57 ^{bc}	18.00±0.00 ^c	0.00±0.00 ^e	0.00±0.00 ^b	0.00±0.00 ^c	2.00±0.00 ^c
	3	0.00±0.00 ^e	0.10±0.00 ^{bc}	0.06±0.05 ^c	0.23±0.05 ^a	2.66±0.57 ^b	14.00±0.00 ^{de}	0.00±0.00 ^e	0.00±0.00 ^b	0.00±0.00 ^c	1.00±0.00 ^d
SB	1	15.33±3.05 ^a	0.26±0.05 ^a	0.23±0.05 ^a	0.23±0.05 ^a	4.66±0.57 ^a	15.67±0.57 ^{de}	3.00±0.00 ^c	1.00±0.00 ^a	0.00±0.00 ^c	1.00±0.00 ^d
	2	0.00±0.00 ^e	0.13±0.05 ^{bc}	0.13±0.05 ^{abc}	0.10±0.00 ^b	2.66±0.57 ^b	50.00±0.00 ^a	15.00±0.00 ^a	1.00±0.00 ^a	2.33±0.57 ^a	6.33±1.15 ^a
	3	4.66±0.57 ^e	0.16±0.05 ^b	0.10±0.00 ^{bc}	0.00±0.00 ^e	2.33±0.57 ^{bc}	16.00±0.00 ^d	0.00±0.00 ^e	0.00±0.00 ^b	0.00±0.00 ^c	1.00±0.00 ^d
RB	1	11.00±1.00 ^d	0.06±0.05 ^{cd}	0.13±0.05 ^{abc}	0.00±0.00 ^e	1.33±0.57 ^c	26.00±0.00 ^b	2.00±0.00 ^d	1.00±0.00 ^a	1.00±0.00 ^b	3.00±0.00 ^b
	2	8.33±2.08 ^b	0.06±0.05 ^{cd}	0.13±0.05 ^{abc}	0.10±0.00 ^b	0.06±0.05 ^c	0.00±0.00 ^f	0.00±0.00 ^e	0.00±0.00 ^b	0.00±0.00 ^c	0.00±0.00 ^e
	3	0.00±0.00 ^e	0.10±0.00 ^{bc}	0.13±0.05 ^{abc}	0.13±0.05 ^b	2.00±0.00 ^{bc}	26.00±0.00 ^b	2.00±0.00 ^d	0.00±0.00 ^b	0.00±0.00 ^c	2.66±0.57 ^b
PL		10.00	0.60	2.00	0.02	1.30	10.00	0.60	2.00	0.02	1.30
Sources of variation		Level of significance									
Biochar* Percentage		*	*	*	*	*	*	*	*	*	*

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$ (DMRT). **PL** –Permissible Limit (Source: World Health Organisation, 1996). Unit in mg/kg. **StB** – Standard Biochar, **SB** – Sorghum Biochar, **RB** –Rice Biochar, **Trts** – Treatments

Table 28: Effect of different concentrations of biochars on heavy metal content in root of *Pennisetum glaucum* in 2018 and 2019

Trts	Rate (%)	2018					2019				
		Cu	Zn	Pb	Cd	Cr	Cu	Zn	Pb	Cd	Cr
Control	0	7.66±1.15 ^b	0.11±0.02 ^{bc}	0.21±0.02 ^{ab}	0.15±0.00 ^{ab}	0.18±0.05 ^d	17.33±1.15 ^a	0.33±0.57 ^b	1.00±0.00 ^a	0.00±0.00 ^a	2.00±0.00 ^a
StB	1	0.66±0.57 ^{de}	0.06±0.05 ^{cd}	0.13±0.05 ^{bcd}	0.16±0.05 ^a	1.66±0.57 ^{bc}	10.00±0.00 ^c	0.00±0.00 ^b	0.00±0.00 ^b	0.00±0.00 ^a	0.00±0.00 ^c
	2	0.00±0.00 ^e	0.06±0.05 ^{cd}	0.13±0.05 ^{bcd}	0.00±0.00 ^d	1.33±0.57 ^c	6.00±0.00 ^{ef}	0.00±0.00 ^b	0.00±0.00 ^b	0.00±0.00 ^a	0.00±0.00 ^c
	3	0.00±0.00 ^e	0.20±0.00 ^a	0.16±0.05 ^{abc}	0.13±0.05 ^{ab}	2.00±0.00 ^{abc}	11.33±1.15 ^c	1.00±0.00 ^a	0.00±0.00 ^b	0.00±0.00 ^a	1.00±0.00 ^b
SB	1	18.00±2.00 ^a	0.16±0.05 ^{ab}	0.23±0.05 ^a	0.10±0.00 ^{abc}	0.00±0.00 ^d	14.00±0.00 ^b	0.00±0.00 ^b	0.00±0.00 ^b	0.00±0.00 ^a	1.00±0.00 ^b
	2	4.66±1.15 ^c	0.06±0.05 ^{cd}	0.10±0.00 ^{cd}	0.03±0.05 ^{cd}	2.33±0.57 ^{ab}	4.66±1.15 ^f	0.00±0.00 ^b	0.00±0.00 ^b	0.00±0.00 ^a	0.00±0.00 ^c
	3	1.66±0.57 ^{de}	0.03±0.05 ^{cd}	0.06±0.05 ^{de}	0.06±0.05 ^{bcd}	2.66±0.57 ^a	8.00±0.00 ^d	0.00±0.00 ^b	0.00±0.00 ^b	0.00±0.00 ^a	0.00±0.00 ^c
RB	1	4.66±1.15 ^c	0.06±0.05 ^{cd}	0.10±0.00 ^{cd}	0.06±0.05 ^{bcd}	0.00±0.00 ^d	0.00±0.00 ^g	0.00±0.00 ^b	0.00±0.00 ^b	0.00±0.00 ^a	0.00±0.00 ^c
	2	0.33±0.57 ^e	0.00±0.00 ^d	0.00±0.00 ^e	0.13±0.05 ^{ab}	2.33±0.57 ^{ab}	6.66±1.15 ^{de}	0.00±0.00 ^b	0.00±0.00 ^b	0.00±0.00 ^a	0.00±0.00 ^c
	3	2.33±0.57 ^d	0.00±0.00 ^d	0.06±0.05 ^{de}	0.06±0.05 ^{bcd}	0.00±0.00 ^d	16.66±1.15 ^a	0.00±0.00 ^b	0.00±0.00 ^b	0.00±0.00 ^a	1.00±0.00 ^b
PL		10.00	0.60	2.00	0.02	1.30	10.00	0.60	2.00	0.02	1.30
Sources of variation		Level of significance									
Biochar*		*	*	*	*	*	*	*	*	*	*
Percentage											

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$ (DMRT). **PL** –Permissible Limit (Source: World Health Organisation, 1996). Unit in mg/kg. **StB** – Standard Biochar, **SB** – Sorghum Biochar, **RB** –Rice Biochar, **Trts** – Treatments

Table 29: Effect of different concentrations of biochars on heavy metal content in shoot of *Pennisetum glaucum* in 2018 and 2019

Trts	Rate (%)	2018					2019				
		Cu	Zn	Pb	Cd	Cr	Cu	Zn	Pb	Cd	Cr
Control	0	11.00±1.00 ^b	0.13±0.05 ^{ab}	0.10±0.00 ^b	0.13±0.05 ^{cd}	3.00±0.00 ^{ab}	18.00±0.00 ^b	1.00±0.00 ^a	1.00±0.00 ^a	0.00±0.00 ^b	2.00±0.00 ^a
StB	1	0.00±0.00 ^e	0.00±0.00 ^d	0.16±0.05 ^{ab}	0.20±0.00 ^{bc}	0.00±0.00 ^d	21.33±1.15 ^a	1.00±0.00 ^a	1.00±0.00 ^a	1.00±0.00 ^a	2.00±0.00 ^a
	2	11.33±1.15 ^b	0.13±0.05 ^{ab}	0.26±0.05 ^a	0.26±0.05 ^b	3.33±0.57 ^a	11.33±1.15 ^d	0.00±0.00 ^b	0.00±0.00 ^b	0.00±0.00 ^b	1.00±0.00 ^b
	3	4.00±1.00 ^d	0.13±0.05 ^{ab}	0.06±0.05 ^b	0.16±0.05 ^{cd}	2.33±0.57 ^{bc}	11.33±1.15 ^d	0.00±0.00 ^b	0.00±0.00 ^b	0.00±0.00 ^b	1.00±0.00 ^b
SB	1	8.66±1.15 ^{bc}	0.00±0.00 ^d	0.13±0.05 ^b	0.20±0.00 ^{bc}	1.66±0.57 ^c	8.00±0.00 ^e	0.00±0.00 ^b	0.00±0.00 ^b	0.00±0.00 ^b	0.00±0.00 ^c
	2	7.00±1.00 ^c	0.03±0.05 ^{bc}	0.13±0.05 ^b	0.20±0.00 ^{bc}	0.00±0.00 ^d	22.00±0.00 ^a	1.00±0.00 ^a	1.00±0.00 ^a	1.00±0.00 ^a	2.00±0.00 ^a
	3	6.66±1.15 ^{cd}	0.06±0.05 ^{abc}	0.10±0.00 ^b	0.16±0.05 ^{cd}	3.00±0.00 ^{ab}	16.66±0.57 ^b	1.00±0.00 ^a	0.00±0.00 ^b	0.00±0.00 ^b	2.00±0.00 ^a
RB	1	19.33±4.16 ^a	0.16±0.05 ^a	0.06±0.05 ^b	0.36±0.05 ^a	3.33±0.57 ^a	17.33±1.15 ^b	0.00±0.00 ^b	0.00±0.00 ^b	0.00±0.00 ^b	2.00±0.00 ^a
	2	10.33±0.57 ^b	0.13±0.05 ^{ab}	0.10±0.00 ^b	0.13±0.05 ^{cd}	2.00±0.00 ^c	14.00±0.00 ^c	0.00±0.00 ^b	0.66±0.57 ^a	1.00±0.00 ^a	1.00±0.00 ^b
	3	11.00±1.00 ^b	0.10±0.10 ^{abc}	0.26±0.05 ^a	0.10±0.00 ^d	3.66±0.57 ^a	8.00±0.00 ^e	0.00±0.00 ^b	0.00±0.00 ^b	0.00±0.00 ^b	0.00±0.00 ^c
PL		10.00	0.60	2.00	0.02	1.30	10.00	0.60	2.00	0.02	1.30
Sources of variation		Level of significance									
Biochar* Percentage		*	*	*	*	*	*	*	*	*	*

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$ (DMRT). **PL** –Permissible Limit (Source: World Health Organisation, 1996). Unit in mg/kg. **StB** – Standard Biochar, **SB** – Sorghum Biochar, **RB** –Rice Biochar, **Trts** – Treatments

Table 30: Effect of different concentrations of biochars on heavy metal content in soil after planting *Tithonia diversifolia* in 2018 and 2019

Trts	Rates (%)	2018					2019				
		Cu	Zn	Pb	Cd	Cr	Cu	Zn	Pb	Cd	Cr
Control	0	0.00±0.00 ^f	0.06±0.05 ^{ab}	0.10±0.00 ^{bc}	0.00±0.00 ^b	1.00±0.00 ^d	15.33±1.15 ^d	1.00±0.00 ^c	0.00±0.00 ^b	0.00±0.00 ^b	1.00±0.00 ^d
StB	1	5.00±2.00 ^d	0.13±0.05 ^{ab}	0.10±0.00 ^{bc}	0.16±0.05 ^a	1.00±0.00 ^d	0.00±0.00 ^e	0.00±0.00 ^d	0.00±0.00 ^b	0.00±0.00 ^b	0.33±0.57 ^d
	2	0.00±0.00 ^f	0.10±0.00 ^{ab}	0.10±0.00 ^{bc}	0.13±0.05 ^a	2.33±0.57 ^{bc}	31.33±1.15 ^a	6.00±0.00 ^a	1.00±0.00 ^a	1.00±0.00 ^a	4.00±0.00 ^a
	3	8.66±0.57 ^{ab}	0.06±0.05 ^{ab}	0.13±0.05 ^{abc}	0.16±0.05 ^a	1.33±0.57 ^d	24.67±1.15 ^b	0.00±0.00 ^d	0.00±0.00 ^b	0.00±0.00 ^b	2.66±0.57 ^b
SB	1	6.66±1.15 ^e	0.10±0.00 ^{ab}	0.16±0.05 ^{ab}	0.16±0.05 ^a	3.33±0.57 ^{ab}	23.33±1.15 ^b	0.00±0.00 ^d	0.00±0.00 ^b	0.00±0.00 ^b	3.00±0.00 ^b
	2	0.00±0.00 ^f	0.03±0.05 ^b	0.06±0.05 ^c	0.00±0.00 ^b	2.33±0.57 ^{bc}	20.00±0.00 ^c	1.00±0.00 ^c	0.00±0.00 ^b	0.00±0.00 ^b	2.00±0.00 ^c
	3	1.33±1.15 ^{ef}	0.13±0.05 ^{ab}	0.06±0.05 ^c	0.00±0.00 ^b	2.66±0.57 ^{bc}	20.00±0.00 ^c	2.66±0.57 ^b	0.00±0.00 ^b	0.00±0.00 ^b	2.00±0.00 ^c
RB	1	9.33±1.15 ^a	0.16±0.05 ^a	0.20±0.00 ^a	0.13±0.05 ^a	3.66±0.57 ^a	0.00±0.00 ^e	0.00±0.00 ^d	0.00±0.00 ^b	0.00±0.00 ^b	0.00±0.00 ^e
	2	7.33±1.15 ^{bc}	0.10±0.10 ^{ab}	0.13±0.05 ^{abc}	0.13±0.05 ^a	2.33±0.57 ^c	20.00±0.00 ^c	0.33±0.57 ^d	0.00±0.00 ^b	0.00±0.00 ^b	0.00±0.00 ^e
	3	1.66±0.57 ^e	0.06±0.05 ^{ab}	0.13±0.05 ^{abc}	0.00±0.00 ^b	2.33±0.57 ^{bc}	0.00±0.00 ^e	0.00±0.00 ^d	0.00±0.00 ^b	0.00±0.00 ^b	0.00±0.00 ^e
PL		10.00	0.60	2.00	0.02	1.30	10.00	0.60	2.00	0.02	1.30
Sources of variation		Level of significance									
Biochar*		*	*	*	*	*	*	*	*	*	*
Percentage											

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$ (DMRT). **PL** –Permissible Limit (Source: World Health Organisation, 1996). Unit in mg/kg. **StB** – Standard Biochar, **SB** – Sorghum Biochar, **RB** –Rice Biochar, **Trts** – Treatments

Table 31: Effect of different concentrations of biochars on heavy metal content in root of *Tithonia diversifolia* in 2018 and 2019

Trts	Rates (%)	2018					2019				
		Cu	Zn	Pb	Cd	Cr	Cu	Zn	Pb	Cd	Cr
Control	0	0.00±0.00 ^d	0.00±0.00 ^d	0.10±0.00 ^c	0.06±0.05 ^{bc}	1.33±0.57 ^c	0.33±0.57 ^g	0.00±0.00 ^b	0.00±0.00 ^a	0.00±0.00 ^c	0.00±0.00 ^c
StB	1	3.33±0.57 ^b	0.16±0.05 ^a	0.06±0.05 ^{cd}	0.10±0.00 ^b	0.00±0.00 ^d	0.00±0.00 ^g	0.00±0.00 ^b	0.00±0.00 ^a	0.00±0.00 ^c	0.00±0.00 ^c
	2	10.66±1.15 ^a	0.13±0.05 ^{ab}	0.23±0.05 ^a	0.23±0.05 ^a	3.66±0.57 ^a	10.00±0.00 ^d	0.00±0.00 ^b	0.00±0.00 ^a	0.00±0.00 ^c	1.00±0.00 ^b
	3	0.00±0.00 ^d	0.00±0.00 ^d	0.06±0.05 ^{cd}	0.00±0.00 ^c	1.66±0.57 ^{bc}	5.66±0.57 ^e	0.00±0.00 ^b	0.00±0.00 ^a	0.00±0.00 ^c	0.50±0.00 ^c
SB	1	1.66±0.57 ^c	0.00±0.00 ^d	0.06±0.05 ^{cd}	0.00±0.00 ^c	3.66±0.57 ^a	20.00±0.00 ^a	0.00±0.00 ^b	0.00±0.00 ^a	0.00±0.00 ^c	2.00±0.00 ^a
	2	3.33±1.15 ^b	0.00±0.00 ^d	0.00±0.00 ^d	0.00±0.00 ^c	1.33±0.57 ^c	11.00±0.00 ^c	1.00±0.00 ^a	0.50±0.00 ^a	0.83±0.28 ^b	1.00±0.00 ^b
	3	1.33±1.15 ^{cd}	0.06±0.05 ^{bcd}	0.10±0.00 ^c	0.10±0.00 ^b	2.66±0.57 ^{ab}	0.00±0.00 ^g	0.00±0.00 ^b	0.00±0.00 ^a	0.00±0.00 ^c	0.00±0.00 ^c
RB	1	0.00±0.00 ^d	0.16±0.05 ^a	0.20±0.00 ^{ab}	0.13±0.05 ^b	2.33±1.15 ^{bc}	0.00±0.00 ^g	0.00±0.00 ^b	0.00±0.00 ^a	0.00±0.00 ^c	0.00±0.00 ^c
	2	4.66±1.15 ^b	0.10±0.00 ^{abc}	0.10±0.00 ^c	0.13±0.05 ^b	2.00±0.00 ^{bc}	4.00±0.00 ^f	0.00±0.00 ^b	0.00±0.00 ^a	0.00±0.00 ^c	0.00±0.00 ^c
	3	3.33±1.15 ^b	0.03±0.05 ^{cd}	0.13±0.05 ^{bc}	0.13±0.11 ^b	1.66±0.57 ^{bc}	14.00±0.00 ^b	0.00±0.00 ^b	0.00±0.00 ^a	2.33±0.57 ^a	1.00±0.00 ^b
PL		10.00	0.60	2.00	0.02	1.30	10.00	0.60	2.00	0.02	1.30
Sources of variation		Level of significance									
Biochar*		*	*	NS	*	*	*	*	*	*	*
Percentage											

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$ (DMRT). **PL** –Permissible Limit (Source: World Health Organisation, 1996). Unit in mg/kg. **StB** – Standard Biochar, **SB** – Sorghum Biochar, **RB** –Rice Biochar, **Trts** – Treatments

Table 32: Effect of different concentrations of biochars on heavy metal content in shoot of *Tithonia diversifolia* in 2018 and 2019

Trts	Rates (%)	2018					2019				
		Cu	Zn	Pb	Cd	Cr	Cu	Zn	Pb	Cd	Cr
Ctrl	0	9.33±1.15 ^{ab}	0.03±0.05 ^{bc}	0.76±1.06 ^a	0.13±0.05 ^{bc}	2.00±0.00 ^{bcd}	18.00±0.00 ^b	1.00±0.00 ^a	0.00±0.00 ^a	0.00±0.00 ^b	2.00±0.00 ^b
StB	1	3.66±0.57 ^{ef}	0.00±0.00 ^c	0.10±0.00 ^b	0.13±0.05 ^{bc}	0.06±0.05 ^f	0.00±0.00 ^h	0.00±0.00 ^b	0.00±0.00 ^a	0.00±0.00 ^b	0.00±0.00 ^c
	2	0.66±0.57 ^h	0.00±0.00 ^c	0.00±0.00 ^b	0.00±0.00 ^d	2.33±0.57 ^{bc}	25.33±1.15 ^a	0.00±0.00 ^b	0.00±0.00 ^a	0.00±0.00 ^b	3.00±0.00 ^a
	3	10.00±2.00 ^a	0.13±0.05 ^a	0.16±0.05 ^{ab}	0.13±0.05 ^{bc}	2.66±0.57 ^{ab}	5.66±0.57 ^f	0.00±0.00 ^b	0.00±0.00 ^a	0.00±0.00 ^b	0.50±0.00 ^c
SB	1	2.00±2.00 ^{fg}	0.13±0.05 ^a	0.13±0.05 ^{ab}	0.10±0.00 ^c	1.33±0.57 ^{de}	7.33±1.15 ^e	0.00±0.00 ^b	0.00±0.00 ^a	0.00±0.00 ^b	0.00±0.00 ^c
	2	4.66±1.15 ^{de}	0.06±0.05 ^{abc}	0.06±0.05 ^b	0.06±0.05 ^{cd}	1.00±0.00 ^e	11.00±0.00 ^d	1.00±0.00 ^a	0.50±0.00 ^a	0.83±0.28 ^a	1.00±0.00 ^b
	3	7.33±0.57 ^{bc}	0.06±0.05 ^{abc}	0.13±0.05 ^{ab}	0.20±0.00 ^{ab}	3.33±0.57 ^a	11.66±0.57 ^d	0.00±0.00 ^b	0.00±0.00 ^a	0.00±0.00 ^b	1.00±0.00 ^b
RB	1	6.66±1.15 ^{cd}	0.10±0.00 ^{ab}	0.10±0.00 ^b	0.20±0.00 ^{ab}	2.00±0.00 ^{bcd}	0.00±0.00 ^h	0.00±0.00 ^b	0.00±0.00 ^a	0.00±0.00 ^b	0.00±0.00 ^c
	2	9.33±1.15 ^{ab}	0.10±0.00 ^{ab}	0.13±0.00 ^{ab}	0.26±0.57 ^a	1.33±0.57 ^{ef}	4.00±0.00 ^g	0.00±0.00 ^b	0.00±0.00 ^a	0.00±0.00 ^b	0.00±0.00 ^c
	3	2.66±0.57 ^{ef}	0.00±0.00 ^c	0.10±0.00 ^b	0.00±0.00 ^d	1.66±0.57 ^{cde}	16.00±0.00 ^c	0.00±0.00 ^b	0.00±0.00 ^a	0.00±0.00 ^b	2.00±0.00 ^b
PL		10.00	0.60	2.00	0.02	1.30	10.00	0.60	2.00	0.02	1.30
Sources of variation		Level of significance									
Biochar*		*	*	NS	*	*	*	*	*	*	*
Percentage											

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$ (DMRT). **PL** –Permissible Limit (Source: World Health Organisation, 1996). Unit in mg/kg. **StB** – Standard Biochar, **SB** – Sorghum Biochar, **RB** –Rice Biochar, **Trts** – Treatments

Table 33: Effect of different concentrations of biochars on heavy metal content in soil of *Tridax procumbens* in 2018 and 2019

Trts	Rates (%)	2018					2019				
		Cu	Zn	Pb	Cd	Cr	Cu	Zn	Pb	Cd	Cr
Control	0	0.00±0.00 ^g	0.00±0.00 ^d	0.10±0.00 ^{cd}	0.13±0.05 ^{bc}	2.00±0.00 ^d	24.00±0.00 ^b	0.00±0.00 ^b	2.33±0.57 ^a	3.00±0.00 ^a	2.66±0.57 ^b
StB	1	3.33±1.15 ^f	0.10±0.00 ^{bc}	0.10±0.00 ^{cd}	0.13±0.05 ^{bc}	2.33±0.57 ^{cd}	0.00±0.00 ^f	0.00±0.00 ^b	0.00±0.00 ^c	0.00±0.00 ^b	0.00±0.00 ^d
	2	5.33±1.15 ^e	0.10±0.00 ^{bc}	0.13±0.05 ^{cd}	0.13±0.05 ^{bc}	1.33±0.57 ^{de}	20.00±0.00 ^{cd}	0.00±0.00 ^b	0.00±0.00 ^c	0.00±0.00 ^b	2.00±0.00 ^b
	3	0.00±0.00 ^g	0.00±0.00 ^d	0.10±0.00 ^{cd}	0.00±0.00 ^d	0.00±0.00 ^e	0.00±0.00 ^f	0.00±0.00 ^b	0.00±0.00 ^c	0.00±0.00 ^b	0.00±0.00 ^d
SB	1	0.00±0.00 ^g	0.03±0.05 ^{cd}	0.10±0.00 ^{cd}	0.10±0.00 ^c	2.66±0.57 ^{cd}	0.00±0.00 ^f	0.00±0.00 ^b	0.00±0.00 ^c	0.00±0.00 ^b	0.00±0.00 ^d
	2	7.33±0.57 ^d	0.06±0.05 ^{bcd}	0.13±0.05 ^{cd}	0.13±0.05 ^{bc}	3.66±0.57 ^b	18.00±0.00 ^d	0.00±0.00 ^b	0.00±0.00 ^c	0.00±0.00 ^b	2.00±0.00 ^b
	3	4.66±1.15 ^{ef}	0.10±0.00 ^{bc}	0.06±0.05 ^d	0.16±0.05 ^{bc}	2.00±0.00 ^d	0.00±0.00 ^f	0.00±0.00 ^b	0.00±0.00 ^c	0.00±0.00 ^b	0.00±0.00 ^d
RB	1	13.33±1.15 ^b	0.20±0.00 ^a	0.23±0.05 ^{ab}	0.26±0.05 ^a	3.66±0.57 ^b	10.00±0.00 ^e	0.00±0.00 ^b	0.00±0.00 ^c	0.00±0.00 ^b	1.00±0.00 ^c
	2	10.00±0.00 ^c	0.13±0.05 ^{ab}	0.16±0.05 ^{bc}	0.20±0.00 ^{ab}	3.00±0.00 ^{bc}	21.33±1.15 ^c	3.00±0.00 ^a	0.00±0.00 ^c	0.00±0.00 ^b	2.00±0.00 ^b
	3	64.66±1.15 ^a	0.13±0.05 ^{ab}	0.30±0.00 ^a	0.10±0.00 ^c	5.66±0.57 ^a	64.66±1.15 ^a	0.13±0.05 ^b	0.30±0.00 ^b	0.10±0.00 ^b	5.67±0.57 ^a
PL		10.00	0.60	2.00	0.02	1.30	10.00	0.60	2.00	0.02	1.30
Sources of variation		Level of significance									
Biochar* Percentage		*	*	*	*	*	*	*	*	*	*

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$ (DMRT). **PL** –Permissible Limit (Source: World Health Organisation, 1996). Unit in mg/kg. **StB** – Standard Biochar, **SB** – Sorghum Biochar, **RB** –Rice Biochar, **Trts** – Treatments

Table 34: Effect of different concentrations of biochars on heavy metal content in root of *Tridax procumbens* in 2018 and 2019

Trts	Rates (%)	2018					2019				
		Cu	Zn	Pb	Cd	Cr	Cu	Zn	Pb	Cd	Cr
Control	0	1.33±0.57 ^b	0.10±0.00 ^c	0.16±0.05 ^a	0.20±0.00 ^a	1.66±0.57 ^a	5.66±0.57 ^a	0.00±0.00 ^a	0.00±0.00 ^a	0.00±0.00 ^b	0.50±0.00 ^a
StB	1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	2	ND	ND	ND	ND	ND	0.00±0.00 ^c	0.00±0.00 ^a	0.00±0.00 ^a	0.00±0.00 ^b	0.00±0.00 ^a
	3	0.00±0.00 ^c	0.00±0.00 ^d	0.00±0.00 ^c	0.00±0.00 ^c	0.00±0.00 ^c	ND	ND	ND	ND	ND
SB	1	0.00±0.00 ^c	0.00±0.00 ^d	0.00±0.00 ^c	0.00±0.00 ^c	0.00±0.00 ^c	ND	ND	ND	ND	ND
	2	0.00±0.00 ^c	0.00±0.00 ^d	0.00±0.00 ^c	0.00±0.00 ^c	0.00±0.00 ^c	0.00±0.00 ^c	0.00±0.00 ^a	0.00±0.00 ^a	0.00±0.00 ^b	0.00±0.00 ^a
	3	0.00±0.00 ^c	0.00±0.00 ^d	0.00±0.00 ^c	0.00±0.00 ^c	0.00±0.00 ^c	1.00±0.00 ^b	0.00±0.00 ^a	0.00±0.00 ^a	0.00±0.00 ^b	0.00±0.00 ^a
RB	1	0.00±0.00 ^c	0.20±0.00 ^a	0.16±0.05 ^a	0.10±0.00 ^b	0.00±0.00 ^c	ND	ND	ND	ND	ND
	2	2.66±0.57 ^a	0.10±0.00 ^c	0.03±0.05 ^c	0.10±0.00 ^b	1.66±0.57 ^a	5.66±0.57 ^a	0.00±0.00 ^a	0.00±0.00 ^a	0.00±0.00 ^b	0.50±0.00 ^a
	3	0.00±0.00 ^c	0.16±0.05 ^b	0.10±0.00 ^b	0.06±0.11 ^{bc}	1.33±0.57 ^{ab}	6.00±0.00 ^a	0.00±0.00 ^a	0.00±0.00 ^a	2.33±0.57 ^a	0.50±0.00 ^a
PL		10.00	0.60	2.00	0.02	1.30	10.00	0.60	2.00	0.02	1.30
Sources of variation		Level of significance									
Biochar* Percentage		*	*	*	NS	*	*	*	*	*	*

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$ (DMRT). **PL** –Permissible Limit (Source: World Health Organisation, 1996). Unit in mg/kg. **StB** – Standard Biochar, **SB** – Sorghum Biochar, **RB** –Rice Biochar, **Trts** – Treatments, **ND** – Not Determined

Table 35: Effect of different concentrations of biochars on heavy metal content in shoot of *Tridax procumbens* in 2018 and 2019

Trts	Rates (%)	2018					2019				
		Cu	Zn	Pb	Cd	Cr	Cu	Zn	Pb	Cd	Cr
Control	0	1.66±0.57 ^b	0.20±0.00 ^a	0.16±0.05 ^a	0.10±0.00 ^{ab}	1.66±0.57 ^b	5.66±0.57 ^a	0.00±0.00 ^a	0.00±0.00 ^a	0.00±0.00 ^a	5.00±0.00 ^a
StB	1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	2	ND	ND	ND	ND	ND	0.00±0.00 ^c	0.00±0.00 ^a	0.00±0.00 ^a	0.00±0.00 ^a	0.00±0.00 ^a
	3	0.00±0.00 ^c	0.00±0.00 ^c	0.00±0.00 ^c	0.00±0.00 ^c	0.00±0.00 ^c	ND	ND	ND	ND	ND
SB	1	0.00±0.00 ^c	0.00±0.00 ^c	0.00±0.00 ^c	0.00±0.00 ^c	0.00±0.00 ^c	ND	ND	ND	ND	ND
	2	0.00±0.00 ^c	0.00±0.00 ^c	0.00±0.00 ^c	0.00±0.00 ^c	0.00±0.00 ^c	0.00±0.00 ^c	0.00±0.00 ^a	0.00±0.00 ^a	0.00±0.00 ^a	0.00±0.00 ^a
	3	0.00±0.00 ^c	0.00±0.00 ^c	0.00±0.00 ^c	0.00±0.00 ^c	0.00±0.00 ^c	1.00±0.00 ^b	0.00±0.00 ^a	0.00±0.00 ^a	0.00±0.00 ^a	0.00±0.00 ^a
RB	1	12.00±2.00 ^a	0.03±0.05 ^c	0.13±0.05 ^{ab}	0.13±0.05 ^a	3.66±0.57 ^a	ND	ND	ND	ND	ND
	2	1.66±0.57 ^b	0.10±0.00 ^b	0.13±0.05 ^{ab}	0.03±0.05 ^{bc}	1.00±0.00 ^b	5.66±0.57 ^a	0.00±0.00 ^a	0.00±0.00 ^a	0.00±0.00 ^a	0.50±0.00 ^a
	3	0.00±0.00 ^c	0.13±0.05 ^b	0.06±0.05 ^{bc}	0.06±0.11 ^{abc}	1.66±0.57 ^b	6.00±0.00 ^a	0.00±0.00 ^a	0.00±0.00 ^a	0.00±0.00 ^a	0.50±0.00 ^a
PL		10.00	0.60	2.00	0.02	1.30	10.00	0.60	2.00	0.02	1.30
Sources of variation		Level of significance									
Biochar* Percentage		*	*	*	NS	*	*	*	*	*	*

Values are presented as means ± S.D of triplicate values. Values with different superscripts in the same column differ significantly at $p \leq 0.05$ (DMRT). **PL** –Permissible Limit (Source: World Health Organisation, 1996). Unit in mg/kg. **StB** – Standard Biochar, **SB** – Sorghum Biochar, **RB** –Rice Biochar, **Trts** – Treatments, **ND** – Not Determined

4.6. Potential plants for phytoremediation

Table 36 shows bioconcentration factor and the translocation factor of *Zea mays* in 2018 and 2019. In 2018, it was observed that *Zea mays* grown on the soil amended with sorghum biochar and 1% RB had $TF < 1$ for Cu when compared control and other treatments. This renders the plant as an excluder of Cu. However, *Zea mays* grown on the soil amended with 3% RB had the highest TF value (70) which describes the plant as a hyperaccumulator of Cu. The $BCF > 1$ and $TF < 1$ was observed in *Zea mays* on soil amended with 1% RB which indicates that the plant is a potential phytostabilizer of Cu. *Zea mays* on the control soil exhibited BCF and $TF > 1$, hence, a phytoextractor of Cu. All the biochar increased the TF for Zn in *Zea mays* when compared to control. However, 1% STB and RB displayed $TF = 1$ while 1% SB had $TF > 1$, hence describes *Zea mays* as an indicator and accumulator of Zn. In addition, *Zea mays* on soil amended with 2% and 3% RB exhibited the potential to phytostabilize Zn as a result of $BCF > 1$ and $TF < 1$. For Pb, control, 2% StB and 3% RB showed $TF > 1$ in *Zea mays*, hence, a potential accumulator of Pb. However, 3% RB had the highest TF values for Pb. For Cd, *Zea mays* on soil amended with 3% of all the biochars exhibited $TF > 1$ when compared with the control. However, the highest TF was observed in 3% RB. With respect to Cr, 1% and 2% StB, 1% and 3% SB and 2% and 3% RB showed $TF > 1$, thereby describing *Zea mays* as an accumulator. In addition, 3% RB showed BCF and $TF > 1$ for Cr which reveals the plant as a potential phytoextractor. In 2018, TF for Cu increased with increase in rice biochar treatments while Cu decreased with increase in rice biochar in 2019. Rice biochar concentrations resulted to steady decrease in the TF for Zn while TF for Cr increased with increase in rice biochar in year 2018 (Table 36).

In 2019, all the biochars except 2% StB and 3% RB showed $TF > 1$ when compared to the control. However, 1% and 3% StB and SB and 2% RB had BCF and $TF > 1$ for Cu in *Zea mays*.

The BCF and TF >1 for Zn was observed in *Zea mays* grown on soil amended only with 2% RB. *Zea mays* on soil amended with 1% and 3% StB and RB and all levels of SB showed BCF = 1, that is, an indicator for Pb. The TF for Cd was greater than one in *Zea mays* grown on soil amended with 1% and 3% SB. *Zea mays* on control soil exhibited phytostabilizing capability for Cr due to its BCF >1 and TF <1 while BCF and TF >1 was observed in *Zea mays* on soil amended with 1% StB, 1% and 3% SB and 2% RB (Table 36).

Table 37 shows bioconcentration factor and the translocation factor of *Pennisetum glaucum* in 2018 and 2019. In 2018, *P. glaucum* grown on the control soil showed the potential to phytoextract Cu due to its BCF and TF >1 while *P. glaucum* grown on the soil amended with 1% SB achieved BCF >1 and TF <1 that renders the plant as a phytostabilizer of Cu. The 3% StB also described the plant as a phytostabilizer of Zn due to its BCF >1 and TF <1. *P. glaucum* grown on the control and soil amended with 3% StB were described as phytostabilizer of Pb as a result of the BCF >1 and TF <1. *P. glaucum* on the control soil was described as a phytostabilizer of Cd due to BCF >1 and TF <1 while *P. glaucum* on soil amended with 1% StB was classified as a phytoextractor of Cd because it exhibited BCF and TF >1. For Cr, 3% SB showed the plant as phytoextractor (BCF and TF >1) and 2% RB described *P. glaucum* as phytostabilizer due to BCF >1 and TF <1. The TF for Cu, Zn and Pb increased with increase in sorghum biochar (Table 37).

In 2019, the control renders *P. glaucum* as a potential phytoextractor of Cu (BCF and TF >1). *P. glaucum* did not show the potentials to phytoextract Zn, Pb, Cd and Cr (Table 37). Table 38 shows the bioconcentration factor and translocation factor of *Tithonia diversifolia* in 2018 and 2019. It was observed in 2018 that only *Tithonia diversifolia* grown on soil amended with 3% RB was described as a phytostabilizer of Cu because of BCF >1 and TF <1. *Tithonia diversifolia*

grown on soil amended with 1% and 2% StB had the ability to phytostabilize Zn because of its BCF >1 and TF <1. The 2% StB showed the plant as a potential phytostabilizer of Pb (BCF >1 and TF <1) and 3% SB described *T. diversifolia* as a phytoextractor of Pb (BCF and TF >1). For Cd, *T. diversifolia* grown on soil amended with 2% StB exhibited (BCF >1 and TF <1), hence, a potential phytostabilizer. Control and 3% StB showed *T. diversifolia* as a phytoextractor of Cr (BCF and TF >1) while 2% StB and 1% SB showed *T. diversifolia* as a phytostabilizer of Cr (BCF >1 and TF <1) (Table 38). Regardless of the biochar application or otherwise, *T. diversifolia* did not show the potentials to pyto remediate the studied heavy metals in 2019 (Table 38).

Table 39 shows the bioconcentration factor and translocation factor of *Tridax procumbens* in 2018 and 2019. In year 2018, *Tridax procumbens* had no potential to phytoremediate Cu, Pb and Cr. However, 3% RB showed *Tridax procumbens* as a phytostabilizer of Zn (BCF >1 and TF <1) and *Tridax procumbens* on control showed a potential to phytostabilize Cd as a result of its BCF >1 and TF <1 (Table 39).

Regardless of the biochar application or otherwise, *Tridax procumbens* did not show the potentials to pyto remediate the studied heavy metals in 2019 (Table 39). However, 3% RB showed *Tridax procumbens* as a potential phytostabilizer of Cd because of the BCF >1 and TF <1.

Table 36: Effect of different concentrations of biochars on bioconcentration factor (BCF) and transfer factor (TF) of heavy metals in *Zea mays* in 2018 and 2019

Trts	Rates (%)		2018							2019						
			Cu	Zn	Pb	Cd	Cr	AP	EP	Cu	Zn	Pb	Cd	Cr	AP	EP
Control	0	BCF	12.12	0.62	0.46	1.00	0.00	Cu	-	1.56	∞	∞	0.42	2.00	-	Cu, Cr
		TF	1.50	0.00	2.17	0.81	∞			0.84	0.05	0.00	1.00	0.75		
StB	1	BCF	0.33	0.37	0.65	0.50	0.90	-	-	1.76	∞	1.00	1.00	2.00	Cu, Cr	
		TF	2.20	1.00	0.77	0.46	1.22			1.30	16.00	∞	1.00	1.33		
	2	BCF	0.18	0.76	0.46	1.00	0.49	-	-	∞	∞	∞	∞	∞	-	-
		TF	3.19	0.60	1.66	0.77	1.60			0.26	0.00	0.00	0.00	0.20		
	3	BCF	0.55	0.56	0.00	0.38	0.00	-	-	2.61	∞	1.00	1.00	4.00	Cu	-
		TF	1.10	0.77	∞	2.00	∞			1.02	1.66	∞	∞	1.00		
SB	1	BCF	0.24	0.30	0.46	0.76	0.27	-	-	1.64	∞	1.00	∞	2.25	Cu, Cr	-
		TF	0.00	6.67	1.00	1.00	1.30			1.50	1.61	∞	20	1.66		
	2	BCF	0.00	0.00	0.60	1.00	0.00	-	-	∞	∞	1.00	1.00	∞	-	-
		TF	∞	∞	0.46	∞	∞			2.04	5.77	∞	∞	2.25		
	3	BCF	∞	∞	∞	∞	∞	-	-	2.76	∞	1.00	∞	4.00	Cu, Cr	-
		TF	0.25	0.30	0.60	1.23	1.15			2.07	2.88	∞	1.28	2.25		
RB	1	BCF	1.95	1.60	0.37	1.00	1.00	-	Cu	0.41	0.00	1.00	0.00	0.00	-	-
		TF	0.00	1.00	1.00	0.77	1.00			1.80	∞	∞	1.00	∞		
	2	BCF	0.84	1.23	1.30	∞	0.87	-	Zn, Pb	1.60	7	0.00	1.00	2.00	Cu, Zn, Cr	-
		TF	1.29	0.81	0.23	0.00	1.13			1.45	2.57	0.00	∞	1.66		
	3	BCF	∞	1.23	0.76	0.76	1.40	Cr	Zn	1.56	∞	1.00	1.00	1.00	-	Cu
		TF	70.0	0.62	2.30	2.60	1.43			0.76	3.50	∞	1.00	1.16		

AP- Accumulator and phytoextractor (BCF & TF > 1), EP- Excluder and phytostabilizer (BCF > 1 and TF < 1), Indicator, TF = 1

Table 37: Effect of different concentrations of biochars on bioconcentration factor (BCF) and transfer factor (TF) of heavy metals in *Pennisetum glaucum* in 2018 and 2019

Trts	Rate (%)		2018					2019								
			Cu	Zn	Pb	Cd	Cr	AP	EP	Cu	Zn	Pb	Cd	Cr	AP	EP
Control	0	BCF	3.83	0.84	1.61	1.15	0.13	Cu	Pb, Cd	1.08	∞	∞	0.00	1.20	Cu	-
		TF	1.43	1.18	0.45	0.86	16.67			1.03	3.03	1	1.00	1.00		
StB	1	BCF	0.12	∞	1.00	1.60	0.62	Cd	-	0.50	0.00	0.00	0.00	0.00	-	-
		TF	0.00	0.00	1.23	1.25	0.00			2.13	∞	∞	∞	∞		
	2	BCF	0.00	0.37	0.65	0.00	0.80	-	-	0.33	1.00	1.00	1.00	0.00	-	-
		TF	∞	2.17	2.00	∞	2.50			1.88	1.00	1.00	1.00	∞		
	3	BCF	1.00	2.00	2.66	0.56	0.75	-	Zn, Pb	0.80	∞	1.00	1.00	1.00	-	-
		TF	∞	0.65	0.38	1.23	1.17			1.00	0.00	1.00	1.00	1.00		
SB	1	BCF	1.17	0.61	1.00	0.43	0.00	-	Cu,	0.89	0.00	0.00	1.00	1.00	-	-
		TF	0.47	0.00	0.56	2.00	∞			0.57	1.00	1.00	1.00	0.00		
	2	BCF	∞	0.46	0.76	0.30	0.87	-	-	0.09	0.00	0.00	0.00	0.00	-	-
		TF	1.52	0.50	1.30	0.67	0.00			5.50	∞	∞	∞	∞		
	3	BCF	0.35	0.18	0.60	∞	1.14	Cr	-	0.50	1.00	1.00	1.00	0.00	-	-
		TF	4.12	5.33	1.67	2.67	1.13			2.00	∞	1.00	1.00	∞		
RB	1	BCF	0.42	1.00	0.76	∞	0.00	-	-	0.00	0.00	0.00	0.00	0.00	-	-
		TF	4.10	2.16	0.60	6.00	∞			∞	1.00	1.00	1.00	∞		
	2	BCF	0.03	0.00	0.00	1.30	38.83	-	Cr	∞	1.00	1.00	1.00	1.00	-	-
		TF	31	∞	∞	1.00	0.87			2.10	1.00	∞	∞	∞		
	3	BCF	∞	0.00	0.46	0.46	0.00	-	-	0.64	0.00	1.00	1.00	0.37	-	-
		TF	4.78	∞	4.33	1.67	∞			0.48	1.00	1.00	1.00	0.00		

AP- Accumulator and phytoextractor (BCF & TF > 1), EP- Excluder and phytostabilizer (BCF > 1 and TF < 1), Indicator, TF = 1

Table 38: Effect of different concentrations of biochars on bioconcentration factor (BCF) and transfer factor (TF) of heavy metals in *Tithonia diversifolia* in 2018 and 2019

Trts	Rates (%)		2018							2019						
			Cu	Zn	Pb	Cd	Cr	AP	EP	Cu	Zn	Pb	Cd	Cr	AP	EP
Control	0	BCF	1.00	0.00	1.00	∞	1.33	Cr	-	0.02	0.00	1.00	1.00	0.00	-	-
		TF	∞	∞	7.60	2.16	1.50			54.54	∞	1.00	1.00	∞		
StB	1	BCF	0.66	1.23	0.60	0.62	0.00	-	Zn	1.00	1.00	1.00	1.00	0.00	-	-
		TF	1.09	0.00	1.66	1.30	∞			1.00	1.00	1.00	1.00	1.00		
	2	BCF	∞	1.30	2.30	1.76	1.57	-	Zn,Pb,Cd,Cr	0.31	0.00	0.00	0.00	0.25	-	-
		TF	0.06	0.00	0.00	0.00	0.64			2.53	1.00	1.00	1.00	3.00		
	3	BCF	0.00	0.00	0.46	0.00	1.24	Cr	-	0.22	1.00	1.00	1.00	0.18	-	-
		TF	∞	∞	2.67	∞	1.60			1.00	1.00	1.00	1.00	1.00		
SB	1	BCF	0.24	0.00	0.37	0.00	1.09	-	Cr	0.85	1.00	1.00	1.00	0.66	-	-
		TF	1.25	∞	2.16	∞	0.36			0.36	1.00	1.00	1.00	0.00		
	2	BCF	∞	0.00	0.00	1.00	0.57	-	-	0.55	1.00	∞	∞	0.50	-	-
		TF	1.38	∞	∞	∞	0.75			1.00	1.00	1.00	1.00	1.00		
	3	BCF	1.00	0.46	1.66	∞	1.00	Pb	-	0.00	0.00	1.00	1.00	0.00	-	-
		TF	5.51	1.00	1.30	2.00	1.25			∞	1.00	1.00	1.00	∞		
RB	1	BCF	0.00	1.00	1.00	1.00	0.63	-	-	1.00	1.00	1.00	1.00	1.00	-	-
		TF	∞	0.62	0.50	1.53	0.85			1.00	1.00	1.00	1.00	1.00		
	2	BCF	0.63	1.00	0.76	1.00	0.85	-	-	0.20	0.00	1.00	1.00	1.00	-	-
		TF	2.03	1.00	1.30	2.00	0.66			1.00	1.00	1.00	1.00	1.00		
	3	BCF	2.00	0.50	1.00	∞	0.71	-	Cu	∞	1.00	1.00	∞	∞	-	-
		TF	0.78	0	0.77	0	1.0			1.14	1.00	1.00	0.00	2.00		

AP- Accumulator and phytoextractor (BCF &TF> 1), EP- Excluder and phytostabilizer (BCF >1 and TF <1), Indicator, TF=1

Table 39: Effect of different concentrations of biochars on bioconcentration factor (BCF) and transfer factor (TF) of heavy metals in *Tridax procumbens* in 2018 and 2019

Trts	Rates (%)		2018							2019						
			Cu	Zn	Pb	Cd	Cr	AP	EP	Cu	Zn	Pb	Cd	Cr	AP	EP
Control	0	BCF	∞	∞	1.60	1.53	0.83	-	Cd	0.23	1.00	0.00	0.00	0.18	-	-
		TF	1.24	2.00	1.00	0.50	1.00			1.00	1.00	1.00	1.00	10.00		
StB	1	BCF	ND	ND	ND	ND	ND	-	-	ND	ND	ND	ND	ND	-	-
		TF	ND	ND	ND	ND	ND			ND	ND	ND	ND	ND		
	2	BCF	ND	ND	ND	ND	ND	-	-	0.00	1.00	1.00	1.00	0.00	-	-
		TF	ND	ND	ND	ND	ND			1.00	1.00	1.00	1.00	1.00		
	3	BCF	1.00	1.00	0.00	1.00	1.00	-	-	ND	ND	ND	ND	ND	-	-
		TF	1.00	1.00	1.00	1.00	1.00			ND	ND	ND	ND	ND		
SB	1	BCF	1.00	0.00	0.00	0.00	0.00	-	-	ND	ND	ND	ND	ND	-	-
		TF	1.00	1.00	1.00	1.00	1.00			ND	ND	ND	ND	ND		
	2	BCF	0.00	0.00	0.00	0.00	0.00	-	-	0.00	1.00	1.00	1.00	0.00	-	-
		TF	1.00	1.00	1.00	1.00	1.00			1.00	1.00	1.00	1.00	1.00		
	3	BCF	0.00	0.00	0.00	0.00	0.00	-	-	∞	1.00	1.00	1.00	1.00	-	-
		TF	1.00	1.00	1.00	1.00	1.00			1.00	1.00	1.00	1.00	1.00		
RB	1	BCF	0.00	1.00	0.69	0.38	0.00	-	-	ND	ND	ND	ND	ND	-	-
		TF	∞	0.15	0.81	1.30	∞			ND	ND	ND	ND	ND		
	2	BCF	0.26	0.76	0.18	0.50	0.55	-	-	0.26	0	1.00	1.00	0.25	-	-
		TF	∞	0.15	0.81	1.30	∞			ND	ND	ND	ND	ND		
	3	BCF	0.00	1.23	0.33	0.60	0.23	-	Zn	0.09	0.00	0.00	23.3	0.10	-	Cd
		TF	0.00	0.81	0.60	1.00	1.24			1.00	1.00	1.00	0.00	1.00		

AP- Accumulator and phytoextractor (BCF & TF > 1), EP- Excluder and phytostabilizer (BCF > 1 and TF < 1), Indicator, TF=1

CHAPTER FIVE

DISCUSSION

The biochar produced locally in this study was crispy in texture and black in color which proved its name “Black Carbon”. Production yield for standard (wheat) biochar, sorghum biochar and rice biochar are 23.54%, 36.37% and 30% respectively. The result of production yield of rice biochar in this study is in agreement with that of Kamara *et al.* (2015) who revealed production yield (29.7%) of rice biochar. Production yield of biochar is determined by the production temperature and resident time (Wu *et al.*, 2012). Correspondingly, Sadaka *et al.* (2014) reported slight reductions in production yield of switchgrass biochar from $35.5\% \pm 0.3\%$ to $35.2\% \pm 0.6\%$ pyrolysed at 400°C with elevated residence time from 2 h to 3 h. Similar results were reported in wheat-straw (32.40–22.8 %) by Gai *et al.* (2014). Also, O’toole *et al.* (2013) revealed production yield ($24 \pm 4.7\%$) of wheat biochar. The result of this study was in agreement with Sadaka *et al.* (2014) opinion which stated that decreased in the production yield result from increase in temperature and residence time. Standard biochar obviously showed the decreased production yield. This could be as a result of the decomposition of the lignocellulosic material. The differences between the production yield of rice biochar and sorghum may be as a result of the feedstock type.

Many biochars have been reported to have alkaline pH (Gaskin *et al.*, 2008; Spokas *et al.*, 2012; Wu *et al.*, 2012; Zhao *et al.*, 2017). Stella Mary *et al.* (2016) reported elevated pH (8.84–9.84) of biochars. Alkaline nature with pH (9.3) was discovered in the rice straw biochar produced (Kamara *et al.*, 2015). Sigua *et al.* (2015) also revealed high pH (13.0) of sorghum biochar pyrolyzed at 500°C. Similarly, this study showed the alkaline nature of the biochars (rice, sorghum

and standard biochar) with pH values (8.15-8.54). The alkaline nature of these biochars could result from the presence of carbonates formation (such as CaCO_3 and MgCO_3) and inorganic alkalis (such as K) (Yuan *et al.*, 2011; Ding *et al.*, 2014). Conforming to Ding *et al.* (2014), they confirmed that the primary cause of alkaline biochar was the separation of the alkali salt from the organic materials. This indicates that the alkaline biochar pyrolysed from high temperature can enhance the acidic soil by promoting the formation of metal hydroxide precipitation and heavy metals adsorption (Ahmad *et al.* 2014).

Qian *et al.* (2013) reported low moisture content (1.10-1.99%) in sorghum biochar. From Bouqbis *et al.* (2016) study, the low moisture content (0.97%) in argan shell biochar was observed. He *et al.* (2019) showed reduction in moisture content with increase in the pyrolysis temperature. In line with He *et al.*'s (2019) work, this study revealed moisture content value of 3.48% for standard biochar pyrolysed at 700°C. However, moisture content of 4.13% and 5.75% were observed for rice and sorghum biochars pyrolysed at 550°C. Moreover, moisture content of sorghum and rice biochars were higher than standard biochar. Low moisture in biochar is necessary as a result of reduction in the heat energy and required time for the pyrolysis (Tripathi *et al.*, 2016). The reduced moisture content in biochars indicate its ability to become more polyaromatic and graphite-like in nature as a result of longer pyrolysis time (Darmstadt *et al.*, 2000). Cybulak *et al.* (2016) noted that biochar applied to soil raises the moisture content of the soil by about 1.5–3.0% which benefit the dry and degraded soils. Videgain-Marco *et al.* (2020) reported that biochar pyrolysed at 400 had moisture content value of 0.57% and the other biochar pyrolysed at 600 had moisture content value of 3.05%.

Varying ash and volatiles content of biochar could result from the type of feedstocks and pyrolysis temperature (Antal *et al.*, 2003; Guerrero *et al.*, 2008). The result of this study revealed

that volatile content increased in rice biochar (550°C) followed by standard biochar (700°C) and sorghum biochar (550°C). Pyrolysis temperature affect the biochar structure as a result of volatile matter that is released (Shaaban *et al.*, 2014). Increased temperature results to a reduction of volatile matter content (Crombie *et al.*, 2013; Kambo and Dutta, 2015; Tag *et al.*, 2016). Zhao *et al.* (2017) reported that higher pyrolysis temperature led to a decrease in the volatile matter content (by 60.8–14.9%) for biochars derived from apple tree branches. Ronsse *et al.* (2012) opined that the increased temperature led to a further cracking of the volatile fractions into low-molecular-weight liquids and gases instead of biochar. Moreover, increasing pyrolysis temperature may lead to the water removal of hydroxyl groups and thermal decomposition of lignocellulosic biomass (Zhang *et al.*, 2015).

Increasing pyrolysis temperature leads to a rise in the ash contents of biochar (Fuertes *et al.* 2010). Mukherjee *et al.* (2014) discovered that ash content increased after one year and three months of biochar (pyrolysed at low temperature) ageing. Kamara *et al.* (2015) reported 34% ash content of rice straw. Rafiq *et al.* (2016) also showed that increased production temperature led to an elevated ash content (5.7%-18.7%). There was also an increase in ash content with increase in temperature as indicated by Zhao *et al.* (2017). The current study revealed increased ash content in rice (52%) and sorghum biochar (35%) as compared to standard (wheat) biochar (20%) which is similar to Mukherjee *et al.* (2014) report. Gradual increase in the concentration of inorganic and organic materials through combustion may bring about the increase in the ash content (Cao and Harris, 2010; Zhao *et al.*, 2017). Zama *et al.* (2017) further suggested that the increase in biochar nutrients such as Mg, Ca, K, and P may be caused by elevated ash content (ranging from 4.0 to 33.1%).

Mostly, fixed carbon content of biochar elevated with increase in temperature. As the temperature increases, the fixed carbon content changed differently depending on feedstock type (Enders *et al.*, 2012; Ronsse *et al.*, 2013; Tag *et al.*, 2016). Enders *et al.* (2012) discovered that biochar derived from Pine and Oak produced at 600 °C showed the highest fixed carbon contents. Zhao *et al.* (2017) also reported increased fixed carbon (33.60% - 73.50%) with increase in temperature in apple derived biochar. In line with previous study, the present study showed highest value (56.45%) of fixed carbon in standard biochar pyrolyzed at 700°C followed by sorghum biochar (46.63%) and rice biochar (22.11%). Chun *et al.* (2004) suggested that increased carbon content may result from the presence of specific quantity of organic plant materials such as cellulose in the biochar. However, sorghum and rice underwent same pyrolysis temperature of 550°C but their carbon contents varied. This could be as a result of the feedstock type as Enders *et al.* (2012) suggested. From Domingues *et al.* (2017), high carbon content may be as a result of higher degree of polymerization which bring about additional condensed carbon structure in the biochar (Lehmann and Joseph, 2009). On the contrary, Cantrell *et al.* (2012) indicated that the carbon content of biochar derived from chicken droppings reduced with increasing production temperature (ranging from 27.0 to 35.5%). The more the intensity of aromatic structures formed, the stronger the resistant capacity of the biochar to microbial decomposition (Keiluweit *et al.*, 2010).

The atomic ratio of H/C, O/C and (O+N)/C denote the aromaticity, oxidation and polarity of biochar respectively (Cao *et al.*, 2017). Increase in O/C could result from the increase in the surface hydrophilicity i.e the affinity for water molecules (Al-Wabel *et al.*, 2013; Lee *et al.*, 2013; Fang *et al.*, 2014; Doumer *et al.*, 2015). It also indicates the higher oxygen containing functional groups which could result to higher adsorption of heavy metals (Ahmad *et al.*, 2014;

Samsuri *et al.*, 2014; Sun *et al.*, 2014; Zhang *et al.*, 2014). This study reported high O/C (0.24) in sorghum and rice biochars and least (0.19) in wheat biochar. This showed high hydrophilic and adsorption nature in rice and sorghum as compared to wheat biochar. Samsuri *et al.* (2014) also reported high molar ratio of O/C for the empty fruit bunch biochar (0.67) and rice husk biochar (0.37). On the contrary, Wu *et al.* (2012) reported decreased O/C with increase in temperature in rice straw derived biochar. They suggested that it could be caused by the increasing dehydration and decarboxylation reactions thereby pointing out the structures formed which contain condensed carbons like the aromatic rings inferred from FTIR spectra (1600 cm^{-1} , 1038 cm^{-1}).

The major elements included phosphorus, calcium, potassium, and magnesium ($>0.1\text{ wt\%}$) while the minor elements ($<0.1\text{ wt\%}$) included sodium, iron, zinc, copper and other heavy metals (Qian *et al.*, 2013). The major nutrients in this study were found to be greater than $0.1\text{wt\%}$ in all the biochars except for sorghum biochar which has P (0.0%). From the major minerals, K had the highest value for all the biochars though rice biochar had the highest K (11.88). Si, a minor element had the highest value for all the biochars whereas sorghum biochar had the highest (14.72) followed by rice biochar (14.36). According to Zama *et al.* (2017), the increase in phosphorus, calcium, potassium, and magnesium on biochars produced at peak temperatures may be on account of increase in ash content. The toxicants (heavy metals) level determined in the studied biochars were less than the permissible limits recommended by International Biochar Initiatives (IBI, 2012).

SEM study in this research shows the presence and types of pores in sorghum biochar (550°C), rice biochar (550°C) and standard (wheat) biochar (700°C). Pores were observed in the three biochar samples. Porous and skeletal structures of rice biochar were observed which was similar to Zhao *et al.* (2017) who reported porous and skeletal structures in Apple tree orchard biochar

of different temperatures. The fractured pores that exist on the surface of standard (wheat) biochar in this study was comparable to the Kraska *et al.* (2016) report showing the SEM result of wheat straw biochar pyrolyzed at temperature ranging from 350°C-650°C. Wang *et al.* (2017) reported sieve plate like structure of corn straw biochar at 350°C. This type of pore structures was observed in sorghum biochar in this study. Less pores were discovered in the sorghum biochar studied by Qian *et al.* (2013). Slow pyrolysis leads to the liberation of VM, hemicellulose and lignin which had a connection with reduced size, decomposition and fracturing that resulted to extremely different and complex structure of biochar possessing numerous porous structure of different diameters (Pituello *et al.*, 2015; Batista *et al.*, 2018; Wilon, 2019). These result indicates the necessity of the kind of feedstock being one of the key determining factors of biochar features.

FTIR spectra revealed the presence of some functional groups in the three biochars studied. They include: aldehyde (2700cm^{-1}), acetylenic compounds (2200cm^{-1}), carbonyls (2050cm^{-1}), conjugated ketones and quinones (1650cm^{-1}), aliphatic C-O stretch (1050cm^{-1}), aromatics compounds (900cm^{-1} to 885cm^{-1}), halogens (570cm^{-1}) and polysulphides (470cm^{-1}). OH stretch (3400cm^{-1}) and phenolics (1400cm^{-1}) were found in wheat biochar and rice biochar, carboxylic compound (1420cm^{-1}) was found only in sorghum biochar while aliphatic CH stretch (2930cm^{-1}) and thioethers (630cm^{-1}) were found in rice biochar.

Aliphatic compounds reported in this study is in accordance with Wu *et al.* (2012) who revealed presence of aliphatic C-H and C-O in rice straw derived biochar. This indicated the occurrence of dehydration and polymerization and also presence of hemicellulose, cellulose and lignin in the biochars (Ahmad *et al.*, 2012; Wu *et al.*, 2012; Zhao *et al.*, 2017). Rice straw is composed of mainly hemicellulose and cellulose which contributes to the easier decomposition during

pyrolysis as compared to lignin (Yang *et al.*, 2007). This could be associated with the high intensity of aliphatic C-O stretch observed in rice biochar as compared to other biochars in this study. It could also explain the presence of aliphatic C-H stretch found only in rice biochar. Cao *et al.* (2017) also found C-O stretch functional group in rice Hull pyrolysed at 500°C. From this study, aromatic compounds were apparent in all the biochars. High intensity was observed in rice biochar followed by sorghum biochar but least observed in wheat biochar. Surface functional group reduced as the pyrolysis temperature gradually increases (Chen *et al.*, 2018). This could be responsible for the decrease in the surface functional groups of standard (wheat) biochar as compared to rice and sorghum biochar in this study.

Presence of aromatic compounds (C-H) could result to greater dehydration and aromatization in biochars (Wu *et al.*, 2012; Melo *et al.*, 2013). Wu *et al.* (2012) demonstrated the FTIR data which deduced the formation of intermediates and increased aromatization that occurred as rice straw was heated to 400°C and 500°C. He further explained that this result could lead to the tendency of graphene like structure in rice straw biochar. With the tendencies to graphene-like structures at higher temperatures, large quantity of non-C atoms left behind was eliminated. The stability of biochar may be increased for two reasons: the strong formation of Graphene-C and the possibility of accelerated decomposition caused by non-aromatic fraction of biochar through co-metabolism may be declined (Lehmann, 2009). Aromatic systems in double bonds between carbons were observed in this study for all the biochars, which implies the presence of conjugated ketones and quinones. These bonds could also be between carbon and oxygen in amides (Melo *et al.*, 2013).

Carbonyls and aromatic bonds found in peanut hull and pine chip biochar reported by Harris *et al.* (2013) were also observed in all the biochars of this study. The peak 1400cm⁻¹ in wheat and

rice biochar and 1420 cm^{-1} in sorghum biochar denotes presence of phenols and carboxylic salts (Armynah *et al.*, 2018). The peak at 3452 cm^{-1} expected from organic O-H stretching indicates water, hydrogen-bonded hydroxyl in rice husk biochar at temperature range of 250°C - 450°C (Armynah *et al.*, 2018; Claoston *et al.*, 2014). The current study also revealed the hydroxyl compounds present in standard biochar and rice biochar though the intensity was low which could result from loss of hydrogen and oxygen atom due to breaking bond from hydroxyl group (Armynah *et al.*, 2018), which indicated a reduction in polar functional groups as the temperature rises (Zhou *et al.*, 2016). Decrease in the strength of O-H (1325 cm^{-1}) stretching and aromatic C=C and C=O stretching of conjugated ketones and quinones (1600 cm^{-1}) with temperature could propose the degradation of phenols and carboxyls in lignin (Souza *et al.*, 2009).

Observation from the spectra showed bands at 570 cm^{-1} in all biochars due to C-X stretching vibrations which deduced the presence of organo-halogens compounds. The particular halogen detected in this study was aliphatic Iodo compounds. This present result is in consensus with the discovery of Zhao and Narthey (2014) who observed presence of organo-halogens in biochars derived from cotton residue, cotton straw, potato residue, potato straw and swine manure.

Stretching vibrations assigned to S-S linkage appeared at the band of 470 cm^{-1} in all biochars of this study. This showed the presence of polysulphides in the biochars. The weakness of absorption and variability of the position of polysulphide make it have less value in structural determination (Silverstein *et al.*, 2005). Zhao and Narthey (2014) has a similar result related to S-S stretch vibrations with peak between 490.6 and 432.9 cm^{-1} corresponds to disulphide in biochar derived from potato residue, potato straw and cotton residue. C-S stretch vibrations corresponding to thioethers was observed in rice straw biochar of this study. Reverse oxidation and reduction of sulphur group e.g thioethers and polysulphides have primary functions in

enzymes that are involved in regulation of redox reactions. The major sulfur compounds such as the tripeptide glutathione, which helps to detoxify free radicals; phytochelatins and metallothioneins, helps to detoxify heavy metal; and the proteins thioredoxin and ferredoxin, involved in oxidoreduction (Grusak, 2001). The presence of the functional groups in biochars promote ion exchange capacity and nutrient sorption on their surface (Oh *et al.*, 2012; Gul and whalen, 2016).

In this current study, the soil porosity increased in response to the incorporation of biochar treatment. This finding is in agreement with Blanco-Canqui. (2017) who indicated that biochar applied to soil improved the soil porosity by 2 to 41%. He further pointed out that in a linear manner, soil porosity improved with an increase in biochar application. From Omondi *et al.* (2016) study, biochar application boosted soil porosity by 8.4%. According to Blanco-Canqui, biochar can promote soil porosity by increasing soil aggregates, influencing mineral soil particles, and reducing soil packing. From the study of Sun and Lu (2014), it was shown that biochar application had a positive influence on soil porosity. Adekiya *et al.* (2020) also reported high porosity in soil after biochar was introduced. Appearance of biochar particles with improved porous nature possess beneficial result on porosity of soil (Jones *et al.*, 2010; Mukherjee and Lal, 2013; Walters and White, 2018). Several studies revealed that high porous nature of biochar could result from its high pyrolysis temperature. In this regard, Andrenelli *et al.* (2016) noted that porous nature of soil was not influenced by the addition of wheat bran derived biochar produced at 800°C. However, soil porosity was enhanced with the application of wheat bran derived biochar produced at 1200°C. Low density of biochar could contribute to its significant and positive influence on soil porosity (Blanco-Canqui, 2017). Blanco-Canqui further pointed out that sandy soils respond quickly to biochar addition than clay soil. The improved

porous nature of soil in response to biochar application can improve the movement of water, heat, and gases in the soil. However, high soil compaction declined aeration, water movement, root growth, and crop yield. Little compaction enhances root–soil association and pore connection, thereby boosting the richness of nutrients and water transport to roots (Arvidsson, 1999).

Porosity of biochar determines its water holding capacity (Yu *et al.*, 2006; Ogawa and Okimori, 2010; Berek, 2014; Yang *et al.*, 2015) because they alter pore characteristics. Novak *et al.* (2009), Lei and Zhang (2013) and Albuquerque *et al.* (2014) confirm biochars produced at high pyrolysis temperature increased water holding capacity following application of biochar thereby increasing crop yield. It was also revealed by Sun *et al.* in 2014 that straw derived biochar may positively influence the water holding capacity of soils. Karhu *et al.* (2011) and Adekiya *et al.* (2020) quoted that application of biochar increases soil water holding capacity. Similarly, the current study revealed an increase in soil water holding capacity with addition of biochars. In contrast, Jeffery *et al.* (2015) discovered that grass derived biochar declined soil water retention. The existence of pores (intrapores) in the biochar particles may create more room for reserving water beyond the pore space between soil particles (interpores) (Masiello *et al.*, 2015). Sohi *et al.* (2009) mentioned that the biochar surfaces pyrolysed at low temperatures have high hydrophobicity and therefore the soil water storage capacity is limited. Hydrophobicity of biochar varies with pyrolysis temperature and feedstock (Kinney *et al.*, 2012; Wang *et al.*, 2013), but is usually removed by environmental exposure. They further pointed out that high hydrophobicity of the biochar could be responsible for the decrease. However, Kinney *et al.* (2012) noted grass derived biochar to have low hydrophobicity in comparison to wood biochars. This study revealed presence of pores and high hydrophilicity (i.e low hydrophobicity) in all the

studied biochars, hence, contributed to the increase in water retention capacity. Water retention has also been found to improve in soil after biochar addition (Chan *et al.*, 2008; Downie *et al.*, 2009; Lehmann and Joseph, 2009). As a result of improved surface area and porous nature of biochar, soil texture and soil aggregation can be improved to increase water retention (Asai *et al.*, 2009; Brockhoff *et al.*, 2010; Verheijen *et al.*, 2010; McElligott *et al.*, 2011).

pH is one of the important properties of soil that enhances nutrient retention and availability (Steiner *et al.*, 2007). There have been positive reports on some biochars increasing soil pH. It was further explained that these biochars which increase soil pH could act as liming materials thereby improving plant growth (Novak *et al.*, 2009; Van Zwieten *et al.*, 2010). Several studies have also reported soil pH increase in response to biochar application (Chan *et al.*, 2008; Masulili *et al.*, 2010; Peng *et al.*, 2011; Kamara *et al.*, 2014; Lu *et al.*, 2014; Zhao *et al.*, 2017; Si *et al.*, 2018). Similarly, report from this work showed that the soil treated with biochars had higher pH than the control. This indicates that the biochars had a positive influence on the soil pH. Yang *et al.* (2015) also revealed increase in pH level of soil with application of bamboo and rice straw. An increase in ash content of biochar has positive effect on pH, that results to increase available nutrient and its uptake in plant (Glaser *et al.*, 2002; Lehmann and Rondon, 2006; Lehmann and Joseph, 2009). The result of this study revealed that soil pH increased due to increased ash content of the biochars used.

Ndor *et al.* (2015) noted that soil moisture content increased after the applications of rice husk and sawdust biochars. Adekiya *et al.* (2020) also indicated a positive influence of biochar on soil moisture. It has been shown that biochar has the ability to elevate moisture in the soil (Ajema, 2018 and Tokova *et al.*, 2020). In line with the previous reports by Ndor *et al.* (2015), Adekiya *et al.* (2020) and Tokova *et al.* (2020), sorghum and rice biochars increased the moisture content in

2018. In addition, 1% and 2% StB and SB, 2% and 3% RB increased soil moisture. Adekiya *et al.* (2020) suggested that presence of micropores in biochar for water retention and soil aggregate improvement leads to creating more pore spaces for earthworm burrowing. In this regard, Tokova *et al.* (2020) supported Adekiya *et al.* (2020) suggestion.

There has been inconsistency of result in several reports made on alleviation and suppression of soil organic matter (SOM) decomposition in soils treated with biochar (Kuzakov *et al.*, 2009; Bolan *et al.*, 2012; Qayyum *et al.*, 2014). Biochars possess higher adsorption capacity for organic matter and may inhibit organic carbon mineralization (Cornelissen *et al.* 2005; Sobek *et al.* 2009). Zimmerman *et al.* (2011) revealed beneficial (< 90 days) and negative (>250 days) effects of grass and wood derived biochars in sandy soils. Similarly, this study revealed that soil organic matter was influenced positively by standard biochar application. Furthermore, organic matter was improved by the biochars in 2019. However, sorghum biochar and rice biochar reduced the soil organic matter in 2018. It was opined by Zimmerman *et al.* (2011) that the negative impact could result from the sorption of native SOM onto the biochars surfaces and pore spaces thereby hindering the SOM from decomposition. Jung (2008) indicated that extremely low (less than 10 %) organic matter is observed in most soils. Furthermore, Kasozi *et al.* (2010) showed that sorption of organic matter onto biochar surfaces is actively restricted by slow diffusion into the small pores of biochar surfaces. On the other hand, there was increase in SOM resulting from biochar treatments incorporation (Glaser *et al.*, 2002; Rawls *et al.*, 2003; Major, 2009; Sohi *et al.*, 2009).

Various organic mineral influence result to accumulation of clay particles and organic materials, which helps in stabilization of soil structure and the carbon compounds within the aggregates (Qayyum *et al.*, 2014). To an extent, researches have been carried out and suggested that there

was increase in the rate at which organic matter decompose after biochar application in soils thus sustains nutrient for plants in temperate region (Awad *et al.*, 2012; Awad *et al.*, 2013; Rogovska *et al.*, 2014). Jien *et al.* (2015) suggested that for biochar pyrolyzed at higher temperature, co-application of biochars with composts may have a positive influence on stabilization of SOM in the soils than individual application. He further deduced from his works that there was a change in the soil structure and formation of some macro-aggregates after biochar addition on soil (Jien and Wang, 2013; Hseu *et al.*, 2014).

Studies have been conducted and showed that biochar can boost soil nutrients (Kammann *et al.*, 2011; Cao *et al.*, 2014; Smider and Singh, 2014; Tammeorg *et al.*, 2014; Stella Mary *et al.*, 2016). Alaboudi *et al.* (2019) showed increase in the soil nutrient in response to biochar application. This study reveals that biochars increase Fe content in the soil when compared to control in both years. However, Mg content was increased by biochar in 2019 which is comparable to the report of Adekiya *et al.* (2020). The P, Ca and K varied in their concentrations in response to the biochars. Biochar retention capacity of nutrients in the soil for crop growth is due to the possession of surface area and porosity (Novak *et al.*, 2009; Liu *et al.*, 2014). Enhancement of soil properties by biochar promotes crop productivity through increasing in nutrient elements (Jha *et al.*, 2010; Albuquerque *e.*, 2014; Ding *et al.*, 2016). In the course of heavy metal adsorption, biochar can adsorb nutrients (Yao *et al.*, 2013; Fang *et al.*, 2014; Mia *et al.*, 2017; Li *et al.*, 2019) which could lead to decrease in the soil nutrients in this study.

According to WHO/FAO (2001), the permissible limits for the following heavy metals in soil are Cu= 100 mg/kg, Zn= 300 mg/kg, Pb= 50 mg/kg, Cd=3 and mg/kg Cr= 100 mg/kg. It was deduced from this study that all the studied heavy metals in the amended soil were lower than the permissible limits. This result is in line with Ekpete and Festus (2013) who reported that Pb, Cu

and Cd concentration levels ranged between 0.669 to 2.624mg/kg; 0.046 to 2.723mg/kg and 0.049 to 0.089mg/kg respectively in automobile contaminated soil. They also deduced from their study that these heavy metals were below the permissible limit. According to Iqbal *et al.* (2011), Cu, Pb and Cd content in soil were within the permissible limit. On the contrary, he concluded that Cr concentration in soil was a threat due to its high values exceeding the permissible limit. Alaboudi *et al.* (2019) also noted high Cr content in the presence of biochar in soil. metals, especially chromium effectively reacts with O₂ and OH ligands at neutral or slightly basic pH to form low solubility oxides and hydroxides, however chromium (VI) forms highly mobile anionic oxides with increased pH (Stengel and Gelin, 2004; Bolan *et al.*, 2013; Choppala *et al.*, 2012).

This study also showed that heavy metals in the amended soil reduced in their concentrations with regards to different concentrations of biochars studied in comparison to the control. This finding is in agreement with previous works carried out on reduction of heavy metal on polluted soil by application of biochars (Beesley *et al.*, 2011; Fellet *et al.*, 2011; Park *et al.*, 2011; Houben *et al.*, 2013; Buss *et al.*, 2016;). Cui *et al.* (2011 and 2012) reported reduction of Cd in technosol after addition of wheat straw derived biochar pyrolyzed at 350°C-550°C. Rice straw biochar also decreased Cu, Cd and Pb in Utisol (Jiang *et al.*, 2012). Same report was made by Zheng *et al.* (2012) who revealed effective reduction of Cd, Pb, Zn and As in Technosol in regards to addition of biochar derived from rice husk, rice straw and rice bran produced at 400°C. Biochar ability to reduce heavy metal could be dependent on its key features such as pH, surface area, carbon and ash content (Lima *et al.*, 2014).

Biochar has the ability to stabilize Pb and Cd and transform them from the labile fraction into less available forms Alaboudi *et al.*, 2019). To a limited extent, biochar pH, especially the higher pH can be the primary cause for the heavy metals reduction found in biochar-amended soils

(Paz-Ferreiro *et al.*, 2014). In the current study, higher pH biochars resulted in soil Cu reduction. In 2019, there was a decrease in Cu with increase in sorghum and rice biochar. On the other hand, Cu increased with increase in standard biochar. This could result from the higher pH in sorghum and rice biochars when compared to that of standard biochar.

Surface sorption of heavy metals on biochar was proved on several cases with the use of scanning electron microscopy (Beesley and Marmiroli, 2011; Lu *et al.*, 2012). It was further explained that the sorption could result from the heavy metals complexation with various functional groups found in the biochar caused by interchange of heavy metals with cations present in biochar, such as Ca^{+2} , Mg^{+2} , K^{+} , Na^{+} and S (Uchimiya *et al.*, 2011c; Lu *et al.*, 2012), or physical adsorption (Lu *et al.*, 2012). In addition, oxygen functional groups are recognized to be responsible for heavy metals stabilization in the biochar surface, mainly for softer acids like Pb^{+2} and Cu^{+2} (Uchimiya *et al.*, 2011c). Sorption mechanism is solely based on type of soil and the cations associated with biochar and soil (Paz-Ferreiro *et al.*, 2014). Recent researches reported that there is electrostatic interaction attraction between biochar and cations (Chen *et al.*, 2011; Regmi *et al.*, 2012). Compounds such as carbonates sulphates and phosphates present in the biochar ash content precipitate with the pollutant for heavy metal stabilization (Cao *et al.*, 2009; Karami *et al.*, 2011; Park *et al.*, 2013). Heavy metal mobilization can be reduced through the alteration of their redox states by biochar such as changing of Cr^{+6} to the less mobile Cr^{+3} (Choppala *et al.*, 2012).

Possession of porous structure, negative charged surface and oxygen-containing functional groups such as phenol, hydroxyl, carbonyl and carboxyl make biochar a better adsorbent for heavy metals (Zhao and Narthey, 2014). High and low pyrolysis temperatures are not only conducive to the formation of functional group, other factors such as the pyrolysis time and raw

materials may also significantly affect the biochar adsorption for different heavy metals (Chen *et al.*, 2018). Decrease in the migration and availability of heavy metals in soil resulted from adsorption and immobilization of heavy metals by biochar which makes it a better alternative to remediate soils polluted with heavy metals.

Different results have been reported as a result of relating soil characteristics, the climatic condition of the site, crop yield to type of feedstocks, pyrolysis conditions, and biochar applications (Sohi *et al.*, 2010). Positive reports from biochar amendment suggested improvement in crop yield (Chan *et al.*, 2007; Albuquerque *et al.*, 2013; Zheng *et al.*, 2013, Ali *et al.*, 2017; Bashir *et al.*, 2018ab). Olmo *et al.* (2014) also investigated that olive-tree -derived biochar amendment improved the wheat growth. On the contrary, Xie *et al.* (2013) found no significant impact on rice grown on non-fertile soil amended with biochar derived from wheat-straw on rice growth in non-fertile soil.

All the biochar treatments did better than the control for plant height of *Zea mays* in 2018 while in 2019, 2% StB and 2% and 3% SB responded positively. The results from the present study was in conjunction with the past reports made concluding that there was increase in maize yield as related to the wheat straw biochar and rice husk biochar applications at various rate (Zhang *et al.*, 2012; Abukari, 2014; Zhang *et al.*, 2014; Zhang *et al.*, 2015; Mensah and Frimpong, 2018). It was observed that *Zea mays* and *Tridax procumbens* height did not respond to rice biochar in 2019 when compared to the result in 2018. This could result from the climate change due to the differences in the time of planting. It may also result from the interaction with the soil type. Biochar effects could depend on its interactions with the soil properties and climatic conditions (Blanco-Canqui, 2017). According to Biederman and Harpole (2013), they explained that in spite of differences in soil type, climate, and production methods, biochar averagely had a neutral to

positive influence on various ecosystem properties. However, same report was revealed in the studies performed by Lehmann *et al.* (2006) and Atkinson *et al.* (2010). For *Pennisetum glaucum* (Pearl millet), its height responded to sorghum and rice biochars. Height of *Tithonia diversifolia* increased with response to 3% SB and all concentrations of rice biochar in comparison to the control and other treatments in 2018 while 1% RB and all concentration of sorghum biochar increased the height of *Tithonia diversifolia* in 2019. The differences in the result of *Pennisetum glaucum* and *Tithonia diversifolia* could be as a result of the opinion made by Blanco-Canqui (2017). Phosphorus availability could result to decrease in plant production (Xie *et al.*, 2013). Among the biochar treatments examined in the current work, rice biochar was observed to increase the height of all the plants studied in 2018.

Result of this study also revealed that rice biochar and sorghum biochar treatments of all concentrations increased the height of *Tridax procumbens* in 2018 and 2019 respectively as compared to control. However, 3% RB and 3% SB had the highest heights for all the studied plants 2018 and 2019 respectively. This result is in accordance with the study of Ghoneim and Ebid (2013) who noted positive response of rice to application of rice straw biochar. He further explained that 3% concentration of rice straw derived biochar did better than other concentration (1.5%) used. Abbas *et al.* (2019) also showed that addition of biochar at 3% improved the height of *Zea mays*. Kamara *et al.* (2014) concluded that rice straw biochar increased the plant height of rice and maize plants with increase in concentration (at the rate of 0.4%, 0.8%, 1.25% and 1.67%). This findings concided with the result of the current study which revealed that height was improved with increase in the concentrations of rice biochar in the studied plants except *Pennisetum glaucum*. With respect to plant height, positive result of rice straw biochar applied on two varieties of rice plants was observed from the report of Kamara *et al.* (2015). According

to Yang *et al.* (2015), rice straw and corn stalk derived biochars increased the yield of peanut, sweet potato and maize plants.

It was reported by Carter *et al.* (2013) that introduction of sorghum biochar increased the leaf number of lettuce and cabbage. Mensah and Frimpong (2018) also had a similar result to that of Carter *et al.* (2013). In contrast to these reports, the present study found out that there was no significant impact of biochars on the leaf number of the *Zea mays* and *Pennisetum glaucum* in 2018. However, the leaf number of *Zea mays* and *Pennisetum glaucum* increased by the biochars in 2019. In 2018, leaf number of *Tithonia diversifolia* was increased by rice biochar but the control had higher values in leaf number in 2019. We could still say that the improved leaf number of the plants in this study still correspond to the positive result of leaf number obtained from the study of Carter *et al.* (2013), and Mensah and Frimpong, (2018). Necrosis was observed in the studied plants (*Tithonia* and *P. glaucum* treated with 1% SB and *Zea mays* treated with 1% and 2% RB). High heavy metal concentrations could lead to necrosis in plants as opined by Waqas *et al.* (2014) who revealed mild necrosis in soybean after being stressed by high level of Zn. The leaf number of *Tridax procumbens* was improved by rice biochar in 2018 as compared to control and other biochars but in 2019, there was no significant difference between the control and the biochars.

This study revealed increased leaf area of *Zea mays* grown on biochars when compared to those on the control in 2018. The leaf area of *Pennisetum glaucum* was improved by 3% of all biochars in 2018 while 2% and 3% of rice and sorghum biochars improved the leaf area in 2019. *Tithonia diversifolia* grown on soil amended with rice biochar in 2018. Only 3% RB boosted the growth of *Tridax procumbens* in 2018. Generally, rice biochar especially at 3% concentration had the highest leaf area in all the plants studied in 2018. The results of this study corresponds with Tian

et al. (2017) who revealed positive response of leaf area of Asian Lotus (*Nelumbo nucifera*) and Chinese sage (*Salvia miltiorrhiza*) to application of biochar. Agegnehu (2017) also showed that biochar enhanced the leaf area of barley. He further explained that the changes in the soil properties like high water retention, increased macronutrients, soil pH and available phosphorus and possibly potassium contents in soil.

It was observed in this study that biochars increased the stem girth of *Zea mays* in 2018. Also, biochars increased the stem girth of *Tithonia diversifolia* when compared to the control. This agrees with Mensah and Frimpong (2018) who reported increase in stem girth of two maize varieties in Aiyinase soil after application of corncobs derived biochar pyrolyzed at 350°C. However, rice biochar with 3% concentration recorded the highest stem girth in *Zea mays*. In 2019, stem girth of *T. diversifolia* increased with increase in the concentrations of rice biochar and trendy increase was noticed in stem girth of *Zea mays* by sorghum biochar. This agrees with the report made by Kamara *et al.* (2014) stating that maize and rice (main tiller) stem girths increased with increasing application levels of biochars made from maize stover and rice straw for certain period. This result still agrees with Carter *et al.* (2013) who explained that there was increase in the stem girth of lettuce and cabbage after introduction of sorghum biochar at the rate of 50g/kg. However, rice biochar and sorghum biochar with 3% concentration had the best influence on *Zea mays* and *T. diversifolia*. Necrosis of *Zea mays* plant treated with rice biochar with 1% and 2% was observed. Stem girth of *P. glaucum* without treatment (Control) was found to do better than the *P. glaucum* treated with all the biochar treatments in 2018. Kamara *et al.* (2014) also explained that further biochar introduction to maize and rice plant did not increase the stem girth i.e control did better at the end of the experiment (week 3 and week 4). Although,

all the biochars at 2% and 3% did better in 2019. Necrosis was also observed in the pearl millet treated with sorghum biochar 1%.

From the report of this study and other research, we could deduce positive and negative response of plants to different biochars with respect to their growth parameters. Though, the percentage of the positive result was more than 50%. In general, rice biochar and sorghum biochar performed better than standard biochar. Biochar has been reported to boost plant growth and yield (Chan *et al.*, 2007; Zheng *et al.*, 2010; Onwuka and Nwangwu, 2016). In accordance with Genesio *et al.* (2012), physical conditions change with biochar; its dark color alters thermal dynamics and alleviates quick plant germination, creating more time for growth compared with controls. The distribution of elemental composition in biochars, such as Ca and K, is known to be a key property when used as an amendment agent due to their function in improving plant growth (Qian *et al.*, 2013). Production of feedstock is recognized to generate biochar with high pH, carbon, CEC, and exchangeable cations (Masulili *et al.*, 2010; Wu *et al.*, 2012; Milla *et al.*, 2013) which make such biochar a potential soil amendment (Kamara *et al.*, 2015). The high pH and mineral contents (P, Ca, K, and Mg) in the studied biochars could result to their performance on the growth of the studied plants. Mensah and Frimpong (2018) suggested from his study that high pH in soil and P availability could contribute to plant growth. From Jeffery *et al.*'s (2017) study, it showed that biochar can be a useful to the improvement of plant growth and yield. Considering the result obtained from the properties of rice biochar and sorghum biochar, it could be deduced that these properties favoured the soil properties and growth of the plants studied and thereby considered as the best soil amendments among the other biochars studied.

This study revealed that all biochars increased the root length of *Zea mays* and *P. glaucum* as compared to control. Among the biochars, wheat biochar had the highest root length in *Zea mays*

and rice biochar had the highest root length in *P. glaucum*. Though, *Tithonia* root length was recorded to be higher in control than the biochar treatments. However, 3% RB and SB recorded longest root in 2018 and 2019 respectively. The current study supports the work of Bruun *et al.* (2014) who revealed that biochar boosts the plant biomass. Waines (2012) connected increased root growth with yield for some wheat cultivars. Farhangi-Abriz and Torabian (2018) also reported improvement of root length bean plant (*Phaseolus vulgaris*) in response to biochar application.

Root growth is dependent on water-holding capacity (WHC) and bulk density of soil (Crutchfield, 2016). Biochar can regulate soil water-holding capacity (Laird *et al.*, 2010), thereby increasing plant biomass (Kammann *et al.*, 2011). Bruun *et al.* (2014) further explained that the improved biomass result from increased water holding capacity and reduced soil bulk density by biochar. Though, high water holding capacity results to a waterlogged environment where plants tend to have reduced number of roots. Biochar applications is able to decrease water holding capacity of soil from 9% to 15% due to the biochar type and the soil (Dugan *et al.*, 2010; Karhu *et al.*, 2011; Basso *et al.*, 2013). According to Crutchfield (2016), wheat (*Triticum aestivum* L.) plants have the tendency to increase in root growth when grown with biochar. Root biomass in barley increased when similar rates of biochar (1% by weight) were applied in sandy soils, although there is a corresponding increase in yield (Bruun *et al.*, 2014).

Carter *et al.* (2013) revealed positive response of rice husk biochar addition on the aboveground biomass and belowground biomass of lettuce and cabbage in a sandy, acidic soil of Cambodia. His report suggested that rice husk biochar has important potential benefits for both subsistence and commercial agriculture. Sigua *et al.* (2015) also discovered favourable effects of sorghum biochars on aboveground and belowground biomass of winter wheat. Rice straw biochar

addition improved the shoot and root biomass of two varieties of rice plants (Kamara *et al.*, 2015). Same result was found in Tian *et al.* (2017) who indicated increase in both above ground and belowground biomass of Lotus by adding biochar.

This study revealed a similar result to the previous reports made on positive response of biochars to plant biomass. This study revealed that biochars improved the aboveground biomass of *Zea mays*. For *Pennisetum glaucum*, the aboveground and belowground biomass was improved by the biochars except the shoot fresh weight in 2018. Comparing the results of this study to the report made by other researchers on biochars with respect to plant biomass, we could say that the performance of these biochars favoured the biomass of the studied plants. However, biochar had slight effect on the aboveground and belowground biomass of *Tithonia diversifolia*. Biomass was not recorded for *Tridax* due to its minuteness. Sigua *et al.* (2015) suggested that the neutral to positive response of plant biomass could result from the differences in the rapid and stable reaction of biochars oxidized in the soil is determined by their physico-chemical properties along with the physicochemical conditions of the soil.

Increased pH promotes the formation of precipitates such as CdCO_3 , Cu(OH)_2 , and $\text{Pb}_5(\text{PO}_4)_3\text{OH}$ thereby affecting the mobility of metals in soil (Mousavi *et al.*, 2010; Cao *et al.*, 2011; Lu *et al.*, 2014). Determinants affecting bioavailable metals and their existence in plants are soil pH, SOM, soil texture, and interaction among the target elements (McBride *et al.*, 2004). Metal accumulation by plants can be influenced by some determinants including metal content in soils, soil pH, SOM, types and varieties of plants, and plant life span (Jung, 2008).

After the application of biochar in this experiment, for all the studied plants, the Pb content was lower than the permissible limits of 2.00 mg/kg recommended by WHO (1996) in both years. On

the contrary, Cd and Cr content were higher than the permissible limits of 0.02 mg/kg and 1.30 mg/kg respectively. Iqbal *et al.* (2011) reported lower values of Cu, Pb and Cd content in plants which were within the permissible limit. However, Cr concentration in some plants was a threat due to its high values exceeding the permissible limit. He explained further that for those plants with low metal concentration, increased pH and fine soil texture could help them in the restriction of metal uptake. Alaboudi *et al.* (2019) also confirmed that increased soil pH could be influenced by biochar addition and presence of OH group. Lomaglio *et al.* (2016) also revealed that biochar amendments reduced the content of Pb in *Phaseolus vulgaris* especially in the shoot and he explained that the strong affinity of the plant cell wall could be responsible for the reduced concentration.

This study had similar report with Fosu-Mensah *et al.* (2017) who reported lower Zn content and higher Cd content in the plants when compared with the permissible limit. Wuana *et al.* (2013) also revealed higher Cd content than Pb in *P. glaucum*. The connection of Cd with non-residual fractions of heavy metal which contributes to its mobility and bio-availability to plant (Zhang *et al.*, 2009) could result in the high Cd content in this study. The current study recorded low Cu concentration in *Zea mays* and *P. glaucum* treated with standard and sorghum biochar. Also, *T. diversifolia* recorded low Cu concentrations in all the treatments except 2% of standard biochar. Experiment conducted by Buss *et al.* (2011) and Ahmad *et al.* (2012) on introduction of biochar derived from hardwood forest green waste and oak reduced Cu and Pb content in *Chenopodium quinoa* and the seed germination percentage of *Lactuca sativa* under HMS. In contrast to the result of the current study, Fosu-Mensah *et al.* (2017) confirmed higher content of Pb in their study. In comparison with the permissible limits in the study, there were variations in the heavy metal content with respect to the application rates and biochar used. Hou *et al.* (2017) and Alwi

et al. (2018) opined that differences in metal uptake in plants depend on the plant species and heavy metal types. There was presence of more heavy metals in shoot than in root of the *Zea mays* and *P. glaucum* all through the experiment. This could be as a result of metal ions translocated to the shoot area through the transport network of the plant.

Many plant species that may or may not associate with amendments, have been confirmed good candidates for phytoremediation (Moosavi and Seghatoleslami, 2013). The use of soil amendments in association with plants that possess high heavy metals tolerance can promote phytoextraction and phytostabilization through immobilization of metal(oids) and simultaneously improve the physico-chemical and biological properties of soils (Rees *et al.*, 2015; Sigua *et al.*, 2019). Biochar as one of these amendments has presently been studied for in situ remediation of polluted soils in combination with plants (Beesley *et al.*, 2011; Park *et al.*, 2011; Rees *et al.*, 2015; Novak *et al.*, 2018). There have been contrary results on the effects of amendment agents such as biochars on restriction of heavy metal movement in soil. Previous reports have shown that metal accumulated by plants is determined by the metal type, plant species and the sites (Hou *et al.*, 2017; Leite *et al.*, 2017).

Plants with BCF and TF values greater than 1.0 are referred to as potential phytoextractors (Fitz and Wenzel, 2002) while plants that have high BCF values ($BCF > 1.0$) and low TF ($TF < 1.0$) are considered potential phytostabilizers (Mendez and Maier, 2008; Garba *et al.*, 2013). In this study, control confirmed *Zea mays* and *Pennisetum glaucum* as phytoextractors of Cu and *Tithonia diversifolia* as phytoextractor of Cr. It was observed that the presence of biochar made Cu and Cr unavailable for the plants to either phytoextract or phytostabilize. The result of this study is in agreement with Bashir *et al.* (2018b) who indicated that Cd and Cr availability was reduced in polluted soil due to addition of rice straw derived biochar.

From the result of the study it was observed that control revealed *Pennisetum glaucum*, *Tridax procumbens* and *Zea mays* as phytostabilizers of Cd, Pb and Cd and Cr, respectively. These plants were unable to uptake these metals because of their reduction in the soil. Bashir *et al.* (2019) suggested that the biochar features such as presence of micropores and surface functional groups could be accountable for the reduction of Cr mobility in soil therefore making it impossible for plant to uptake. As reported by Waqas *et al.* (2014), biochar decrease the Zn uptake in soybean shoots and roots. Zn has direct interaction with biochar and is sealed up through specific and nonspecific-adsorption thereby causing a reduction in the level of Zn availability in the soil (Park *et al.*, 2011). Biochar has been used effectively to remediate heavy metal contaminated soils by reducing the concentration in plants grown in the amended soils (Beesley and Marmiroli, 2011; Fellet *et al.* 2011; Choppala *et al.*, 2012; Zhang *et al.*, 2013; Sousa *et al.*, 2018). Biochar addition helps in decreasing the heavy metal intake by most plant species (Karami *et al.*, 2011; Rees *et al.*, 2016; Zheng *et al.*, 2016). Biochars contain SiO_3^{2-} , PO_4^{3-} , CO_3^{2-} and MnO_x particles (Qian and Chen, 2013; Wang *et al.*, 2015b), which form sorption sites with various structure that have strong affinity towards metals thereby forming precipitates such as $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ (Cao *et al.*, 2009), $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ (Ippolito *et al.*, 2012), CdCO_3 and $\text{Cd}_3(\text{PO}_4)_2$ (Zhang *et al.*, 2015). Nzediegwu *et al.* (2019) supported the suggestion made by Offenbacher and PiSunyer (1988) the reduction in Cr mobility could result from the interference with other metals, especially presence of Fe in the soil which may lead to reduction of Cr uptake in plants. In this case, the efficacy of the biochars to reduce heavy metal mobility for plant uptake renders edible plants safe for consumption.

In agreement with Hossain *et al.* (2010) and Dede *et al.* (2012) who revealed that the application of biochars to soil enhanced the phytoextraction and soil properties to meet up the standard

agricultural values of the soils, this study shows that application of biochar improved phytoextraction of Cu and Cr in *Zea mays* in 2019. Also, 3% SB enhanced the phytoextraction of Cr and Pb in *Pennisetum glaucum* and *Tithonia diversifolia*, respectively. Result of Wuana *et al.* (2013) who reported *P. glaucum* to be a good phytoextractor for Cd due to its ability to take up Cd from soil to the shoot coincide with the result of this study which revealed that 3% StB described *P. glaucum* as a phytoextractor of Cd. Increased Cu mobility resulted from the organic matter that was released by biochar (Shen *et al.*, 2018; Wang *et al.*, 2018b). The organic matter released from the biochar bonded with Cu to form organic matter Cu-complexes thereby increasing the mobility of Cu (Meng *et al.*, 2018b).

The result obtained in the present study showed that rice biochar had positive influence on the phytostabilization of Cu, Zn and Pb in *Zea mays*. *Pennisetum glaucum* and *Tithonia diversifolia* had the potential to phytostabilize Cu and Cr, respectively after application of sorghum biochar at 3%. Previous studies demonstrated that biochar has the ability to reduce chromate Cr(VI) contaminated soils under neutral pH through the transformation of hexa-valent chromium Cr(VI) into tri-valent stable form Cr(III) (Choppala *et al.*, 2012; Bolan *et al.*, 2013). From this study, the 3% RB had positive influence on the phytostabilization of Zn and Cd in *Tridax procumbens*. This result is in agreement with the work of other authors like Sigua *et al.* (2019) who showed that biochars improved the phytostabilization of Cd and Zn in corn which is in conjunction with Park *et al.* (2013) and Zhang *et al.* (2013). They confirmed that sorption is one of the mechanisms used in heavy metals retention. Sorption of Cd and Zn in biochars could result from the complexation of the heavy metals with various functional groups that exist in the biochar, such as Ca^{+2} and Mg^{+2} (Lu *et al.*, 2012), K^{+} , Na^{+} and S, or resulting from physical adsorption (Uchimiya *et al.*, 2011). Sigua *et al.* explained further that the high soil pH may contribute to the

enhancement of the phytostabilization of metals through adsorption and complexation of these metals. The certain techniques of restriction of metal movement in the biochar treatments, with high soil pH, was probably the outcome in the formation of precipitates such as $\text{Cd}(\text{OH})_2$ and $\text{Zn}(\text{OH})_2$. Other works revealed the application of biochar and phytostabilization using *Brassica napus* L. at targeted Cd-contaminated soils (Houben *et al.*, 2013). In addition, the observations made by Hartley *et al.* (2009) and Case *et al.* (2014) revealed that biochar can be combined with *Miscanthus* to phytostabilize Cd and Zn in polluted soils. Lebrun *et al.* (2016) also confirmed *Salix alba* as a good phytostabilizer for Pb. The reductions in plant heavy metal concentrations achieved with biochar application varied significantly for different types of plants (Alaboudi *et al.*, 2019).

Conclusion

From the current research, it can be concluded that the studied biochars have the potential to amend degraded soil by improving the soil properties. Generally, biochar application improved the growth of plants in spent oil-contaminated soil. Rice biochar and sorghum biochar improved the plant growth. In addition, biochar has helped in remediating the polluted soil by reducing the heavy metals present. Lower Pb concentration was observed in the studied plants and higher concentration of the studied heavy metals were found in the shoot than in root hence the potential phytoextractor for phytoremediation.

Tridax procumbens was found to be an indicator while other plants were more of accumulators. Studied plants could be either phytoextractor or phytostabilizer depending on their response to biochar treatments. Biochar may enhance soil fertility of soil and plant growth if suitable

application rates are applied. Therefore, biochar and plant remediation can be combined in the remediation of heavy metals contaminated soils for sustainable agriculture and environment.

Major findings

Biochars derived from rice and sorghum straws by slow pyrolysis have physical and chemical properties that are favourably comparable to the standard recommended by International Biochar Initiative (IBI). The functional groups identified in the biochars are relevant for heavy metal adsorption. Biochars demonstrated potentials to amend spent oil contaminated soil by improving soil properties required to support plant growth. Addition of biochars to the soil improved the growth of the studied plants.

Zea mays is a good phytoextractor of Cu and Cr while others plants including, *Pennisetum glaucum*, *Tithonia diversifolia* and *Tridax procumbens* are phytostabilizers of heavy metals even though the heavy metals were lower than the permissible limit, which makes the edible ones harmless for consumption.

Contributions to knowledge

- Indigenous agricultural wastes in Nigeria, particularly sorghum and rice straws are suitable feedstocks for the production of biochar.
- Locally produced biochars have the potential to amend contaminated soils.
- The integrated use of biochar and phytoremediating plants have the potentials to amend contaminated soils.

Recommendations

From the findings of this study, it is recommended that:

1. In promoting a circular economy, rice and sorghum straws should be exploited for the production of biochar. This is a way to optimally utilize plant resources, reduce the waste build up and generate wealth.
2. Biochars should be used to amend contaminated soil to make soil suitable for arable purposes. This is a simple, affordable, feasible and sustainable approach to remediate contaminated soils.
3. Biochar and phytoremediating plants integrated and should be used to adequately amend spent oil contaminated soil.

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