

Comparative characteristics of biochar types from human faecal wastes and pine-bark and sorption of selected heavy metals from effluent and their mobility in an amended loam soil

By

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Submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy in Agriculture (Soil Science)

Soil Science Discipline

School of Agriculture, Earth and Environmental Sciences

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University of KwaZulu-Natal

Pietermaritzburg

South Africa

November 2018

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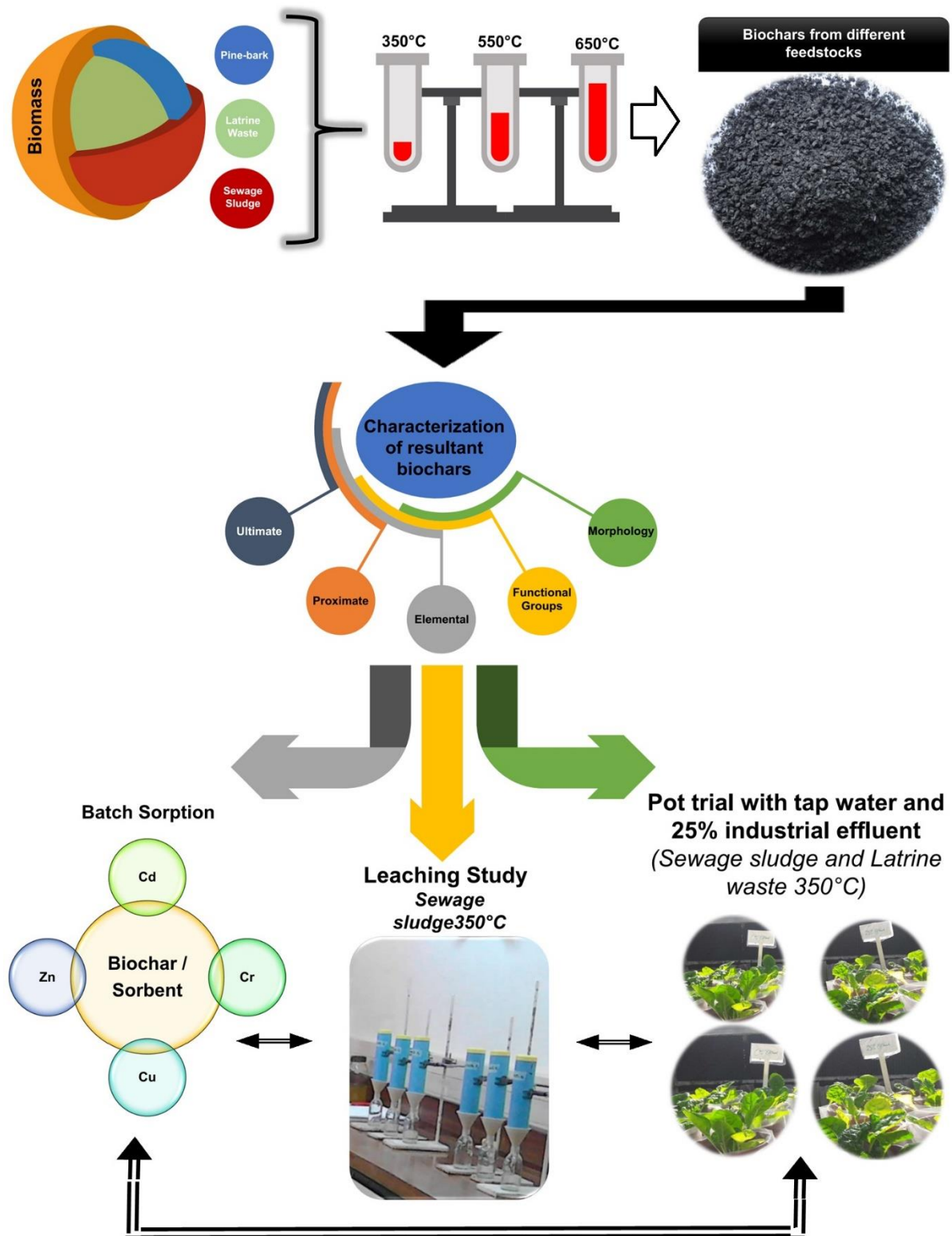
Chapter 3

Koetlisi, K. A., and Muchaonyerwa, P. (2017). Biochar types from latrine waste and sewage sludge differ in physicochemical properties and Cadmium Adsorption. **American Journal of Applied Sciences**, 14 (11), 1039 – 1048. <https://doi.org/10.3844/ajassp.2017.1039.1048>

Chapter 4

Koetlisi A Koetlisi and Pardon Muchaonyerwa. (2018) Pyrolysis Temperature Effects on Yield, Physico-chemical Characteristics of Pine-bark Biochars and Cadmium Sorption. **Indian Journal of Environmental Protection**, 38 (3): 197 – 212 (2018)

Graphical Abstract:



Abstract:

Heavy metals from industrial effluents poses risks to the environment and human health. Pyrolysis of locally available organic wastes could address solid organic waste management and produce a biochar that could immobilise heavy metals in industrial effluents, at source, and in amended soils. Limited research work on characteristics and effectiveness, in addressing environmental challenges, of biochar from latrine waste, sewage sludge and pine bark which are ubiquitous organic wastes in South Africa. The aim of this study were to determine effects of pyrolysis temperature on yield, characteristics and sorption capacities of selected metals from solutions and effluents on biochar from latrine wastes, sewage sludge and pine-bark and on metal mobility in amended soil. The three materials were pyrolysed under limited oxygen at 350, 550 and 650°C. Proximate and ultimate analysis, surface area, porosity and functional groups were analysed on the biochar produced. Batch sorption studies were conducted to determine biochar sorption capacity with Cd, Zn, Cu and Cr in single metal solutions and for Zn, Cu and Cr from a multiple metal solution. A leaching column study was conducted using a loam soil amended with sewage sludge biochar at equivalent rates of 0, 50 and 100 kg ha⁻¹ and the columns leached with industrial effluent while others were leached with distilled water, measuring pH, electrical conductivity, Zn, Cu and Cr in the leachate at each event and in three equal sections of the soil at the end of the experiment. A pot trial was conducted with spinach grown on a loam soil amended at 0, 25, 50 and 100t ha⁻¹ of sewage sludge and latrine waste biochar pyrolysed at 350°C biochars and irrigated with 25% industrial effluent for some and tap water for others. Drymatter, tissue water content, Zn and Cu, and soil pH, EC, Zn and Cu were determined at the end of the trial.

Latrine waste had higher biochar yield, ash content, surface area and pore volume, and lower fixed C and volatile matter than sewage sludge. Biochar yield, volatile matter, total C, N and H decreased with pyrolysis temperature, while ash content, surface area and porosity increased. Surface functional groups of the biochar also varied with feedstock and pyrolysis temperature. The Cd sorption capacities were higher for latrine waste biochar than from sewage sludge. Mixtures of pine bark biochar with latrine waste (1:1) or sewage sludge (1:3) biochar showed synergistic effects on Cd sorption. Sorption capacities of latrine waste, sewage sludge and pine-

bark biochar (350°C) were, respectively, 312.5, 400 and 232.6 mg kg⁻¹ for Zn, 102, 98.0 and 33.3 mg kg⁻¹ for Cu, and 18.9, 13.8 and 67.1 mg kg⁻¹ for Cr from industrial effluent. Conversely, sorption capacities biochar from latrine waste, sewage sludge and pine-bark, respectively, were 278, 227 and 357 mg Zn kg⁻¹, 97.1, 137 and 21.3 mg Cu kg⁻¹, and 122, 106.4 and 147.06 mg Cr kg⁻¹ for single metal solutions. Addition of biochar did not affect shoot drymatter but affected root drymatter and tissue Zn and Cu, with higher Cu than Zn in the tissue. The additions of sewage sludge biochar to neutral, loam soil did not significantly reduce leaching of Cu and Zn from the applied effluent. Moreover, the application of biochar from both latrine waste and sewage sludge increased metal uptake by spinach in the same soil. The findings of this study imply that the characteristics of biochar from latrine waste, sewage sludge and pine bark are different and that faecal waste biochars show positive metal immobilization potential in batch equilibrium studies, but have little or negative effects when added to neutral soils even at extremely high application rates.

Acknowledgements:

I would like to thank God for the continued strength, determination and wisdom. I acknowledge funding from W. K. Kellogg Foundation Southern African Scholarship that supported me to read for a PhD in Agriculture at the University of KwaZulu-Natal until completion. I am much indebted to my supervisor, Professor Muchaonyerwa, for his guidance and support and knowledge sharing during the course of this work. I would like to express my sincere gratitude to Mothae Thapelo and Tamako Ntahbeleng; your courage, kindness and professionalism are what I ought to respect. I acknowledge my fellow post-graduate students and friends for their support in various ways and company, which guaranteed a perfect learning curve in this work: Messrs Vilakazi S.S., Chikuvire T.J., Mdlambuzi T., and Elephant D.E. and Miss Malepfane N.M.

I acknowledge my family, Mesdames Khanyela, J. M., and Qalo-Koetlisi, N. G. M., and Messrs Raporoto, Bulane and Raporoto, S. Matsie, for believing in my dream, undivided and continued support, and encouragement that culminated in the completion of this thesis.

Dedication:

I dedicate this work to my wife Nthabiseng 'Mapabatso Koetlisi Qalo
and my son Pabatso Andreas Koetlisi,
without whom I would not have been decisive and resolute to complete this study.

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CHAPTER 1: INTRODUCTION AND BACKGROUND

1.1 Introduction and Background

Pollution of soil and water with heavy metals poses major risks to the biosphere (Prasad, 1995; Pelleria and Gidarakos, 2015), and human health, through the soil-plant-human pathway (Ghosh and Singh, 2005; Liang et al., 2011). Industrial operations including electroplating and production of batteries, fertilizers and pesticides produce wastewater with high concentrations of heavy metals (Prasad, 1995; Mohan et al., 2007; Perez-Marin et al., 2007). The discharge of the effluents into sewer systems enriches sewage sludge with the metals, which presents challenges for land disposal. This challenge is exacerbated by the occurrence of multiple heavy metals, from different sources, and their non-biodegradability and persistence in the environment (Cui et al., 2015). Treatment of industrial effluent, at source, could make it safer for discharge into the environment (Ranade and Bhandiri, 2014, Gonzalez et al., 2016).

While strategies like precipitation and complexation have been effective in removal of metals from effluents, the specialized reagents and equipment required make them too expensive (Perez-Marin et al., 2007; Shi and Cai, 2009; Mohan et al., 2014). Other potentially effective technologies include membrane filtration, ozonation, advanced oxidation and adsorption (Doble and Kumar, 2005; Ranade and Bhandiri, 2014; Gonzalez et al., 2016), but the high costs also limit their application. Biochar has a potential to be a cost-effective biosorbent for toxic heavy metals from aqueous solutions and wastewater (Namgay et al., 2010; Major, 2011; Kim et al., 2013; Mohan et al., 2014; Coumar et al., 2016). Biochar, a form of charcoal (Lehmann et al., 2003), is a stable carbon-rich product from pyrolysis of plant and animal derived biomass (Ahmad et al., 2013). The effectiveness of biochar in immobilizing heavy metals depends on biochar characteristics owing to properties of the feedstock and pyrolysis conditions (Li et al., 2014; Trakal et al., 2014; Bogusz et al., 2015; Kuppusamy et al., 2016). Feedstocks that have been used for the production of biochar have included forestry waste, crop residues, animal manures and sewage sludge (Ahmed et al.,

2013). Locally available organic waste products, including wood waste, pine-bark, crop residues, animal manure, and human faecal waste among other wastes are potential feedstocks for biochar production. Pine-bark, sewage sludge and latrine wastes are among the most ubiquitous organic wastes in South Africa.

Timber production and wood products industries dispose tonnes of wood and bark wastes throughout the globe annually, resulting leachates with tannic acids, biological oxygen demand, colour and odour from stockpiles to ground-water (Sweet and Fetrow, 1975; Zimms and Berrett, 2004). While the use of wood waste to manufacture particle boards and insulating bats has positive effects on the environment (USDA, 2002; Erlandsson and Sundquist, 2014), the volumes are too large for this beneficial use. Sewage sludge and latrine faecal waste are among the other major organic wastes produced globally and in South Africa.

The global annual production of sewage sludge has increased exponentially over the past decades (Al-Khatib et al., 2010), and the huge quantities, at times with high concentrations of heavy metals originating from contaminated effluents, exacerbate the disposal challenges (Pathak et al., 2009). Where there are no sewer systems, and on-site sanitation systems including pit latrines and septic tanks are used, the disposal of faecal sludge could result in pollution of soil and water resources (Montangero et al., 2002, Vodounhessi and Munch, 2006;). The presence of pathogenic organisms, in human faeces, present a serious threat to human health (Watson and Zakri, 2008).

While incineration of these wastes could aid in energy production and destroys almost all microorganisms, the release of huge volumes of CO₂ and nitrogen and sulphur oxides, makes the practice undesirable (Taiwo, 2011). Whereas landfilling and land application are considered the most economically feasible options (Metcalf and Eddy, 2003), they could contribute to the contamination of soil, water and atmosphere and become a major public health concern (Batool and Ch, 2009; Singh et al., 2011). Landfill may contaminate soils with heavy metals and pathogenic organisms (San and Onay, 2001), and water bodies by leachates and runoff and erosion of elements such as nitrogen and phosphorus, cause eutrophication (Kirkeby et al., 2007; Monfredi and Christensen, 2009). Odours and emissions of CH₄, and nitrous oxides

(San and Onay, 2001; Qdais, 2007), as well as CO₂ from spontaneous fires, could also occur. Sewage sludge and faeces are known to contain plant essential nutrients (Jimenez et al., 2006; Do Thuy et al., 2007), and the insoluble organic matter could restrict the uptake of metals by plants (McBride, 1995), making their land application in agriculture an attractive option. However, the odours and pathogens in these waste products restrict their uses. Production of biochar from these wastes could significantly reduce disposal challenges while possibly producing a valuable product for immobilisation of heavy metals from effluents and in amended soils.

Biochar made from nut shells, plum stones, wheat straws and grape stalks and husks were shown to be highly effective in removal of Cd from aqueous solution (Trakal et al., 2014). Higher pyrolysis temperature has been shown to increase Cd sorption capacity of biochar, possibly as a result of higher aromatic structure, pH and surface area (Kim et al., 2012; Kim et al., 2013). Even though acidic biochar (pH 6.2) has been reported for green waste (Lehmann and Joseph, 2009), biochar commonly has neutral to alkaline pH (Chan et al., 2007). These biochar characteristics are affected by the pyrolysis conditions and feedstock type. There are very few studies on the characteristics of biochar from human faecal wastes (Liu et al., 2014), and comparisons with pine-bark biochar are limited. No studies could be found in the literature on the characteristics of latrine waste biochar. In addition to comparing the characteristics of biochar from these feedstocks, their effectiveness on immobilising metals in solution and in amended soils also needs to be established. Most of the studies on the removal of metals by biochar were done with single metals (Chen et al., 2011; Xu et al., 2013) with fewer on mixtures of metals, at equal concentrations, in aqueous solutions.

The presence of competing metals in aqueous solution, which is often the case in industrial effluents, could affect the sorption of individual metals. Adsorption capacities of metals onto sesame straw biochar were found to be in the order of Pb > Cd > Cr > Cu > Zn from single-metal and Pb > Cu > Cr > Zn > Cd multi-metal solutions (Park et al., 2016). In reality, heavy metals occur at different concentrations in industrial effluents, and the concentration effects may affect the preferential uptake of metals by sorbents. Biochar types that are effective in retaining a variety of metals

from effluents could significantly contribute in the management of industrial effluents. The comparative effects biochar produced from pine-bark, sewage sludge and latrine waste, on retention of multiple metals from effluents, need to be understood.

Biochar has high organic carbon content and hence it can be used as a sustainable soil conditioner to improve soil properties (Glaser et al., 2002). When added to soil, biochar has the potential to directly modify the chemistry, and indirectly modifying physical character, of the soil (Sohi et al., 2009). Soil properties that can be improved by addition of biochar include surface area, aggregate stability (Herath et al., 2013), water holding capacity (Chen, Shinogi and Taira, 2010), pH and CEC (liming effect) (Singh et al., 2010; Major et al., 2010) and sorption and desorption of nutrients and contaminants, with effects on leaching (Sohi et al., 2009; Saarnio, Heimonen and Kettunen, 2013). Effects of soil amendment with biochar from human faecal waste on uptake by plants and leaching of heavy metals in soil irrigated with industrial effluent needs to be understood. There is little-to-no existing literature on the value of biochar from sewage sludge and latrine waste produced at least in Southern Africa.

Chemical composition and pathogen content of human excreta differs by country due to local health, eating habits and sanitizing treatment (Jimenez et al., 2009). The variation in chemical composition of faeces across the world suggest that those from the Southern Africa, and hence the resulting biochar, could be different from those of other regions. Human faecal wastes and pine-bark are among the potential feedstocks for biochar production in South Africa, particularly in KwaZulu-Natal, with high urban and peri-urban population and forestry industry. In addition to these waste products, agricultural and industrial effluents are also produced in large quantities.

1.2 Justification and motivation

The rapidly growing population, global climate change, and pollution are global environmental challenges, which have resulted in water scarcity resulting in the need to utilize non-potable water (Aly, 2016). The water scarcity is exacerbated by pollution of freshwater resources with industrial effluents, including in southern Africa. In recent past, global estimations show that 20 million hectares of arable land have been

irrigated with contaminated water (Trujillo-Gonzalez et al., 2017). Irrigation with contaminated water poses a risk to public health and entire ecosystem due to harmful heavy metals, their toxicity and persistence in the environment (Trujillo-Gonzalez et al., 2017). Deployment of various technologies for decontamination of wastewater (effluent) prior to disposal has been reported (Pathak et al., 2009). Biochar has the ability to immobilize and reduce bioavailability of heavy metals (Manaseri, 2010; Namgay et al., 2010; Mohan et al., 2014), it is imperative to understand the characteristics of biochar from locally available feedstocks (human faecal waste) and pine-bark for immobilisation of heavy metals from industrial effluents.

Like many others, municipalities in KwaZulu-Natal, including the EThekweni Municipality, face challenges in disposal of faecal sludge and heavy metal contaminated effluents. Large stockpiles of sewage and latrine faecal wastes occur at treatment plants in local Municipalities and in the vaults in the case of latrines, respectively, in KwaZulu-Natal. These stockpiles are a threat to the environment and human health. Urine diversion sanitation technology (EcoSan) separates urine from faecal matter to minimize the risk of diseases and pathogenic infections (Peasy, 2000; Vinneras et al., 2006). The differences in management of human faecal wastes between sewage sludge, latrine waste and solid waste from EcoSan toilets suggests that the properties of these wastes and possibly, biochar produced from them, may differ.

These organic materials are believed to contain large quantities of nutrients; their use in agriculture is only limited by pathogen loads, instability resulting in odours and gaseous losses of nutrients. These organic materials may be pyrolysed to biochar, in order to eliminate the challenges, while producing a resource that may result in C sequestration, improving soil quality and health and a cost-effective adsorbent. The woody nature of pine-bark, which is also produced in large quantities in South Africa, could result in biochar that has different characteristics and ability to immobilise heavy metals than biochar from human faecal waste.

These aspects triggered the interest to undertake research to investigate possible and safe use of pine-bark and faecal sludge biochar for removal of heavy metals from the industrial effluents and their immobilisation in an amended soil in the context of

South Africa. The immobilisation of pollutants by biochar from the locally available sewage sludge, latrine waste and pine-bark is anticipated to contribute by minimising pollution of the limited irrigation water resource.

1.3 General Objective

The main aim of this research was to investigate the influence of feedstock and pyrolysis temperature on properties of biochar from sewage sludge, latrine waste and pine-bark from South Africa and their immobilisation of selected heavy metals in effluent and biochar-amended soil through studies on leaching and spinach uptake.

1.3.1 Specific Objectives:

The specific objectives of this study were to determine the effects of:

- I. Pyrolysis temperature and feedstock (latrine waste, sewage sludge and pine-bark) on biochar yield, physicochemical characteristics and Cd sorption capacity
- II. Biochar from human faecal products and pine-bark on sorption of multiple metals from industrial effluent compared to single metals in aqueous solutions.
- III. Sewage sludge biochar rate on immobilization of heavy metals in a loam soil treated with industrial effluent.
- IV. Sewage sludge and latrine waste biochar on biomass production and metal uptake of spinach irrigated with industrial effluent.

Structure of Thesis:

1. Introduction and background
2. Literature Review
3. Biochar types from latrine waste and sewage sludge differ in physicochemical properties and cadmium adsorption
4. Pyrolysis temperature effects on yield, physicochemical characteristics of pine-bark biochars and cadmium sorption
5. Sorption of selected heavy metals with different relative concentrations in industrial effluent on biochar from human faecal products and pine-bark
6. Evaluation of soil amendment with biochar from sewage sludge on heavy metal concentrations in leachates of applied industrial effluent: A leaching column study
7. Dry matter and tissue copper and zinc of spinach grown on a loam soil amended with sewage sludge and latrine waste biochar and irrigated with industrial effluent and tap water
8. General Discussion, Conclusion and Recommendations

CHAPTER 2: LITERATURE REVIEW

2.1 Sources of heavy metal pollution

Metals occur naturally in soils at levels that are generally not toxic (Das et al., 1997). Anthropogenic activities, including mining, fertiliser production, metal plating, battery production and other industrial activities produce effluents enriched with heavy metals (Prasad, 1995; Kabata-Pendias, 2000; Coumar et al., 2016), and increase metal levels in soils and waters. These industrial activities, and land disposal of solid wastes and effluents have increased heavy metal concentrations in the environment (Alloway, 1995; Han et al, 2002; Pinto et al., 2003; Moussa et al. 2006; Duruibe et al., 2007; Ahluwalia and Goyal, 2007). Heavy metal pollution of soils and water poses a serious public health risk. The most toxic and carcinogenic heavy metals include cadmium (Cd), copper (Cu), lead (Pb) and nickel (Ni) (Inyang et al., 2012). Anthropogenic activities in southern Poland were found to increase soil Cd from 2.37 to 26.5 mg kg⁻¹ and Pb from 89.1 to 1,024 mg kg⁻¹ (Biernacka and Maluszynski, 2006). Metal composition of crops/vegetables grown on polluted soils pose serious risks on plant growth and human health (WHO, 2006). Zhou (2003) estimated that the area of agricultural land polluted with Cd, Pb, Cu, and Zn in China was more than 20 million hectares and concentrations of those heavy metals surpassed the national food-safety standards in more than 10 million tons of foodstuffs. Industrial effluent, enriched with heavy metals, is a major cause of pollution of soils and water. There is need to reduce concentrations of soluble metals in effluent and in polluted soils, including altering the physicochemical conditions of soils, including pH and organic matter contents. However, the most effective methods to minimize this pollution would be to remove the metals at the source of the effluents, before disposal. Soil amendments that modify the mobility of the metals in polluted soils could also be essential.

2.2 Approaches to minimise soil and water pollution with heavy metals

The Republic of South Africa, through National Environmental Management Act No. 107 (NEMA, 1998), formulated stringent environmental regulations to guide the removal of heavy metals from the wastewater. Reviewed literature indicates that different methods have been effective for the removal of metals, including precipitation, ion exchange, electrocoagulation, membrane filtration and packed-bed filtration (Inyang et al., 2012; Trakal et al., 2014). Adsorption-based methods are effective for removal of soluble and insoluble organics, inorganic and biological pollutants at up to 99% efficiency (Ali, 2010; Manai et al., 2016). However, these approaches are expensive and the need to use cost-effective methods has resulted in a number of studies using solid organic wastes. Walker et al. (2003) reported that organic amendments of animal manure and humified compost decrease heavy metal bioavailability in soil. There is increasing popularity of biochar derived from organic waste due to the growing challenges of solid waste management, and the need to enhance carbon sequestration and mitigate greenhouse gas emissions (Karhu et al., 2011; Maraseni, 2010). A number of studies have been carried out using biochar, a carbon-rich solid product from thermal pyrolysis of organic biomass under limited oxygen (Dumroese et al., 2011; Downie et al., 2011; Vaughn et al., 2015; Mosa et al., 2016;). Biochar, from organic wastes, has proven to be remarkable as a biosorbent for pollutants through surface adsorption and precipitation mechanisms (Uchimiya et al., 2010; Ahmad et al., 2013; Tan et al., 2015). The most important characteristics of biochar as a sorbent include specific surface area, pore size distribution, surface functional groups and ion-exchange capacity (Ahmad et al., 2013; Jin et al., 2016).

2.3 Biochar and sorption of heavy metals from solution and effluents

Joseph et al. (2010) deduced that high pyrolysis temperature ($> 550^{\circ}\text{C}$) results in biochars that are very recalcitrant to decomposition, high surface area and good adsorbents. Increase in pyrolysis temperature results in low yield of recalcitrant biochar (Hmid et al., 2014; Wang et al., 2015). Surface functional groups of biochar

influence its sorption properties (Amonette and Joseph, 2009). Table 2.1 (single metal) and Table 2.2 (multiple metals) present sorption parameters of different types of biochar used for removal of heavy metals from effluents, based on a systematic review of available literature. This section shows that different biochars differ in their effectiveness due to differences in their characteristics. The section highlights which characteristics make the different biochars effective. Xu et al. (2013) reported that dairy manure biochar sorbed more Cu, Zn and Cd, than biochar from rice husk, when pyrolysed at 350°C. These authors (Xu et al., 2013) observed a similar trend for Pb and Cu from multiple metal solutions, with Pb, Cu, Zn and Cd (Table 2.2). Inyang et al. (2012) also reported that biochar from dairy manure sorbed more Pb and Cu from multiple metal solutions than digested sugar beet (Table 2.2). However, the removal efficiency of Cd and Ni were lower on dairy manure biochar. When pyrolysed at 300, 400, and 505°C, biochar from municipal wastewater sludge (Zhang et al., 2013) appears to sorb more Cr than that produced from rice straw (Qian et al., 2016) (Table 2.1). Based on this part of the review, it appears that biochar from manures and municipal wastewater sludge sorbs higher quantities of metals than biochar derived from plant residues. However, this effect appears to differ between single metal and multiple metal solutions, for some metals.

The Table 2.1 also shows that biochar pyrolysed at 400°C from rice straw and algae-dairy manure sludge had the highest sorption capacity of Cr and Cd (Qian et al., 2016) and Cu (Jin et al. 2016) from single metal solutions than higher or lower temperatures. However, Zhang et al. (2013) found that sorption of Pb and Cr on biochar from municipal wastewater sludge decreased with pyrolysis temperature, with biochar pyrolysed at 300°C sorbing more than 400°C. This trend was also observed by Uchimiya et al. (2010) with biochar from broiler litter. As soil amendments, biochar produced at high pyrolysis temperatures is considered more stable because its recalcitrance originating from higher aromaticity (Kloss et al., 2012). However, based on this reviewed literature on Table 2.1 biochar produced at 400°C or lower could be more effective as biosorbents for immobilising heavy metals in single metal solutions. The most important characteristics of biochar as a sorbent for heavy metals appear to include pH, ash, surface area and surface functional groups.

Table 2. 1: Summary of metal sorption capacities from single metal solutions on biochar produced from different feedstocks and pyrolysis temperatures

Types of biochar	Pyrolysis temperature	Metal elements	Sorption and biochar properties impact	Reference
<i>(i) Plant-derived biochars</i>				
Rice Husk	350	Pb, Cu, Zn & Cd	Metal removal capacity was in the range of 65.5 to 140 mmol kg ⁻¹ attributed to the higher specific surface area. The sorption maxima was 140, 65.5, 101, and 69.5 mmol kg ⁻¹ for Pb, Cu, Zn and Cd respectively.	Xu et al., (2013)
Rice straw	100 300 400 500 700	Cr & Cd	Biochar produced at 400°C was more effective in metal removal due to the presence of oxygen-containing functional groups and mineral matter. The sorption maxima for Cr and Cd was 14.4 and 14.56 mg g ⁻¹ respectively.	Qian et al., (2016)
<i>(ii) Animal manure and municipal solid waste derived biochars</i>				
Algae-dairy manure sludge	400 500 600	Cu	Highest sorption capacity was 21.12mg g ⁻¹ for pristine biochars. When activated, sorption capacity increased to 50.71mg g ⁻¹ . Sorption benefited on biochar surface area and surface functional groups. The lowest pyrolysis temperature of 400°C was the most efficient.	Jin et al., (2016)
Broiler litter manure	350 700	Cd, Cu, Ni & Pb	350°C biochar sorbed more Cu but its surface area was 59.5 m ² g ⁻¹ , 34.7 m ² g ⁻¹ less than that of 700°C. 700°C sorbed more Cd and Ni	Uchimiya et al., (2010)
Dairy manure	350	Pb, Cu, Zn & Cd	Removed all metals above 486 mmol kg ⁻¹ , owing to higher pH and a large amount of mineral elements such as Ca, Mg, K, Al and Fe. The sorption maxima was 555, 496 and 486 mmol kg ⁻¹ for Cu, Zn and Cd respectively.	Xu et al., (2013)
Farmyard and Chicken manure	450	Cu & Zn	Higher sorption, lower C/N ratio. Chicken manure feedstock biochar had highest Cu and Zn sorption of 81.30 and 31.95 mg g ⁻¹ respectively.	Rodriguez-Vila et al., (2018)
Municipal wastewater sludge	300 400 500 600	Pb & Cr	400°C biochar had largest BET surface area and was also rich in organic functional groups leading to highest metal sorption. Sorption maximum and removal efficiencies for Pb and Cr were; 12.6, 18.6, 15.4 and 12.8 mg kg ⁻¹ and 208, 36.6, 45.2 and 19.6 mg kg ⁻¹ at 300, 400, 500 and 600°C respectively	Zhang et al., (2013)

Table 2.2: Summary of metal sorption capacities from multiple metal solutions on biochar produced from different feedstocks and pyrolysis temperatures

Types of biochar	Pyrolysis temp.	Metal elements studied	Sorption and biochar properties impact	Reference
<i>(i) Plant-derived biomass</i>				
Digested beet	sugar 600	Pb, Cu, Ni & Cd	Sorption capacity was best for all metals with 97% removal efficiency. The removal of all metals were greater than 97% in the order of Cd > Ni > Pb > Cu.	Inyang et al., (2012)
Rice Husk	350	Pb, Cu, Zn & Cd	Metal removal capacity was in the range of 65.5 to 140 mmol kg ⁻¹ attributed to the higher specific surface area. The sorption maxima was 79.9 and 27.4 mmol kg ⁻¹ for Pb and Cu respectively.	Xu et al., (2013)
<i>(ii) Animal manure and municipal solid waste derived biochars</i>				
Digested waste	dairy 600	Pb, Cu, Ni & Cd	Digested dairy waste biochar was best for Pb and Cu sorption. The removal of multiple metals was in the order of Pb > Cu > Cd > Ni. Removal efficiencies were 99, 98, 57 and 26% respectively.	Inyang et al., (2012)
Dairy manure	350	Pb, Cu, Zn & Cd	Removed all metals above 486 mmol kg ⁻¹ , owing to higher pH and a large amount of mineral elements such as Ca, Mg, K, Al and Fe. The sorption maxima was 789 and 297 mmol kg ⁻¹ for Pb and Cu respectively.	Xu et al., (2013)

2.4 Biochar for immobilization of heavy metals in polluted soils

Bioavailability and leaching of metals in contaminated soils depends on mineralization of metal-containing organic material and decreasing pH (Rees et al., 2014). Namgay et al. (2010) reported that addition of wood biochar to soil has the ability to immobilize trace elements from the biochar-soil mixture to plants. The addition of prune residue biochar to mine tailings resulted in the reduction of bioavailability and leachability of certain contaminants (Fellet et al., 2011). Shen et al., (2016) reported that biochar reduces the heavy metal content in the plant as a result of immobilization in the soil system. Wagner and Kaupenjohann (2014) found that biochar addition decreased plant Zn and Cd concentrations. Biochar addition potentially reduced bioaccumulation of potentially toxic elements such as As, Cd, Cu, Pb and Zn in the plant tissue of *Brassica rapa* L (Khan et al., 2015). The utilization of biochar as a low-cost sorbent has therefore emerged as a significant alternative (Inyang et al., 2012).

The efficacy of biochar as a sorbent is influenced by feedstock and pyrolysis temperature (Inyang et al., 2011). Masta et al. (2013) evidenced that biochar addition coupled with fly-ash decreased the availability of Cd, Co, Cu, Mn, Ni, Pb, and Zn. In a study that investigated the effect of biochar from manure and lignocelluloses on Zn^{2+} adsorption and desorption, Dai et al. (2016) found that both biochars increased adsorption of Zn^{2+} by the four acidic soil types, and concluded that manure-derived biochar was more effective. Generally, metal adsorption was influenced by the initial metal concentration, pH and biochar type (Dai et al., 2016). Mosa et al. (2016) found that biochar was able to reduce nickel content in tomato. Li et al. (2016) are of the view that long-term effect of biochar on potential toxic elements immobilization depends on biochar properties influenced by feedstock and pyrolysis conditions. Therefore, it is always important to select relevant biochar for specific interest (Roberts and de Nys, 2016). Marginal biomass, described as the material of little or no economic value, makes them interesting for use biochar for use as adsorbents of pollutants and to sequester C and recycle nutrient (Buss et al., 2016).

2.5 Effects of feedstock and pyrolysis conditions on biochar characteristics

The effectiveness on immobilization of heavy metals and on modifying soil quality depends on the intrinsic characteristics of the biochar that are influenced by feedstock type and pyrolysis conditions (Brewer et al., 2011; Luo et al., 2011; Hmid et al., 2014; Jin et al., 2016). A wide range of feedstocks and pyrolysis conditions for production of biochar is reported in the literature (Jeffery et al., 2011). Different types of biomass, including municipal green waste, piggery waste, poultry and human waste, crops and forest residues, paper mill and sawmill waste, can produce biochar (Maraseni, 2010). The feedstocks are dried under solar heat and then oven dried at 75°C (Liu et al., 2014) or 80°C (Yuan and Xu, 2011), before pyrolysis. Pyrolysis temperature is known to significantly influence the properties of the resultant biochar.

Increase in pyrolysis temperature results in a decrease in biochar yield (Lui et al., 2014). Previous reports showed that cellulose, hemicelluloses and lignin are usually thermally degraded between 200°C and 500°C (Maraseni, 2010; Fellet et al., 2011; Mitchell et al., 2013; Baronti et al., 2014). Some studies included higher pyrolysis temperatures up to 600°C (Inyang et al., 2012; Peng et al., 2016; Mosa et al., 2016) and 700°C (Glaser et al., 2002; Luo et al., 2011; Wu et al., 2012; Liu et al., 2014; Wan et al., 2014). Enders et al. (2012) reported that total carbon increased whereas hydrogen and oxygen declined with increase in pyrolysis temperature for production of biochars from wood, crop residues and animal manures. Plant-based biochars mostly contain high C, low contents of total N, P, K, S, Ca, Mg, Al, Na, Cu and metals such as Cu and Zn and as well as low EC and CEC whereas animal-based biochars normally show contradicting trends (Singh et al., 2010).

2.5.1 Plant-derived biochar

Hmid et al. (2014) reported that surface functional groups of olive meal biochar decreased and carbon content increased with an increase in pyrolysis temperature. Table 2.3 shows the effects of increasing pyrolysis temperature on yield, volatile matter, ash content and fixed C and surface area of biochar types from plant-derived

feedstocks. For all biochar types derived from plant residues, biochar yield and volatile matter declined while ash content, surface area and fixed carbon increased with increase in pyrolysis temperature (Table 2.3). The review further shows that biochar yield could decline by 42% and 65% as pyrolysis temperature is creased from 300°C to 700°C for soybean (Ahmad et al., 2012) and pine shaving (Keiluweit et al., 2010), respectively. The table shows that peanut shell, soybean residues and corn stover resulted in lower yield and volatile matter than their woody counterparts in the 300-400°C temperature range. Increasing pyrolysis temperature from 300 to 700°C appears to reduce biochar yield by 30-40% and increase ash content by 0.2-6.6% depending on plant waste used (Table 2.3). There is variation in ash content in corn stover derived biochar ranging 10-58% for 450-550°C and there appears to be no trend with pyrolysis temperature, suggesting that the characteristics of corn stover could have contributed to this difference. Pinewood and pine shavings show showed ash content less than 4%. Within the same range of pyrolysis temperatures, pine wood and shavings resulted in biochar with higher fixed carbon than crop derived biochar (cotton seed hull and corn stover) (Table 2.3). For all the feedstocks reviewed on Table 2.3, the surface area was less than 6 m² g⁻¹ or less for biochar produced at less than 400°C. There is variation in surface area in across feedstocks ranging 0 (cotton seed hull) to 392 m² g⁻¹ (pine shavings) for 400-600°C, no trend with pyrolysis temperature, suggesting that the characteristics of feedstocks contributed to this difference.

Table 2. 3: Summary of proximate analysis and surface area of biochars from various plant-derived feedstocks

Feedstock	Pyrolysis Temp.	Characteristics Yield (%)	Volatile matter (%)	Ash content (%)	Fixed (%)	C	Surface area (m ² g ⁻¹)	Reference
Cottonseed hull	200	83.4	69.3	3.1	22.3	-		Uchimiya et al., (2011c)
	350	36.8	34.9	5.7	52.6	4.7		
	500	28.9	18.6	7.9	67.0	0.0		
	650	25.4	13.3	8.3	70.3	34.0		
	800	24.2	11.4	9.2	69.5	322.0		
Soybean	300	37.03	46.34	10.41	-	5.61		Ahmad et al., (2012)
	700	21.59	14.66	17.18	-	420.3		
Peanut shell	300	36.91	60.47	1.24	-	3.61		
	700	21.89	32.65	8.91	-	448.2		
Pecan shell	350	62	61.6	2.4	-	1.01		Novak et al., (2009)
	700	52	9.7	5.2	-	222		
Corn Stover	500	17.0	-	32.78	-	-		Mullen et al., (2010)
Corn cob	500	18.9	-	13.3	-	-		
Corn Stover	450	15	12.7	58	28.7	12		Lee et al., (2010)
Corn Stover	350	35.0	-	9.8	-	-		Herath et al., (2013)
	550	27.0	-	11.5	-	-		
Pinewood	300	43.7	42.6	0.5	57.4	6		Ronsse et al., (2013)
	450	27.0	16.8	1.2	83.2	23		
	600	23.3	6.4	1.3	93.6	127		
	750	22.7	2.6	1.1	97.4	-		
Pine shaving	100	99.8	77.1	1.2	21.7	1.6		Keiluweit et al., (2010)
	200	95.9	77.1	1.5	21.4	2.3		
	300	62.2	70.3	1.5	28.2	3.0		
	400	35.3	36.4	1.1	62.2	28.7		
	500	28.4	25.2	1.4	72.7	196.0		
	600	23.9	11.1	3.7	85.2	392.0		
	700	22.0	6.3	1.7	92.0	347.0		

2.5.2 Biochar from animal manure and sewage sludge

Huang et al. (2015) indicate that it is technically and economically feasible to use animal manure as feedstock to generate biochar together with heat and power during the pyrolysis process. Table 2.4 shows the effects of increasing pyrolysis temperature on yield, volatile matter, ash content and fixed C and surface area of biochar types from manure-derived feedstocks. Increasing pyrolysis temperature from 300 to 700°C appears to reduce biochar yield by 10-20% for sewage sludge and 20-30% for animal manures (Table 2.4). The same increase pyrolysis temperature appears to increase ash content by 20-36% for sewage sludge and by 15-20% for animal manures. These differences could be explained by the differences in the food/feed that resulted in the production of these feedstocks. The plants that animals feed on tend to have more carbon. Within the 300 - 400°C pyrolysis temperature range sewage sludge biochar appears to have higher surface area than animal manure-derived biochar types (Table 2.4). For biochar type produced at 700°C, plant-derived biochar types had higher surface area (Table 2.3) than biochar from animal manure and sewage sludge. While the trends of different biochar characteristics between sewage sludge, animal manure and plant waste biochar types appear to be clear, their pyrolysis conditions may have been different for each study. Wu et al. (2012) reported that residence time also differs depending on the need for a particular biochar.

The resident time during pyrolysis varied from two hours with dairy, sugar beet wastes and reed residues (Inyang et al., 2012; Peng et al., 2016), through four hours with different plant residues (Yuan and Xu, 2011) to six hours with cottonwood (Mosa et al., 2016). It appears that longer retention time is required during pyrolysis of woody materials than manures. For better comparisons of characteristics, biochar from different feedstocks need to be done at the same pyrolysis temperatures and retention times. This comparison will give a better impression on effects of feedstock and pyrolysis temperature for biochar produced from plant waste, animal manure and human waste (including sewage sludge).

2.5.3 Composition of selected heavy metals in different biochar types

Table 2.5 presents the summary of compositions of selected metals and phosphorus in different biochar types produced under varying pyrolysis temperatures. Cantrell et al. (2012) showed that biochar Cd concentration was lower at higher pyrolysis temperature, using dairy manure, and poultry litter and swine solids. They also reported higher Cd in swine solid biochar than the other two. Different studies (Table 2.5) showed that increasing pyrolysis temperature increased the concentration of Zn, Cu, Cr and P in the biochar. Concentrations of Zn, Cu, Cr and P in biochar was in the order swine solid > sewage sludge > poultry manure > dairy manure, irrespective of pyrolysis temperature (Table 2.5). There were variations in Zn and Cu concentrations in sewage sludge biochar type used by Hossain et al. (2011) in Australia and Zhang et al. (2013) in Guangzhou, China. This may be associated with differences in lifestyle and standard of living in the different regions of the world. In addition, feedstock production attributes and management, and retention time during pyrolysis could also contribute to the difference. Yuan et al. (2016) found that, higher pyrolysis temperature (700°C) sewage sludge biochar contained less N and more P and K and as well as water soluble P and K. A study by Lin et al. (2013) showed that pyrolysis at 220°C resulted in higher concentrations of plant available P and reduced N losses with almost three quarters of initial N from the feedstock retained in the final product. Joseph et al. (2010) are of the opinion that low-temperature pyrolysis favours greater C recovery and to some extent plant nutrients. Hossain et al. (2011) and Cantrell et al. (2012) showed that the pH of biochar from sewage sludge, dairy manure, poultry litter and swine solids increased with pyrolysis temperature in the range 300 – 700°C (Table 2.5). Hossain reported that increasing pyrolysis temperature from 400 to 500°C and from 500 to 600°C increased pH from pH 5 to pH 7, and from 7 to 12, respectively. Biochar from pine wood (Sika and Hardie, 2014), dairy manure, poultry litter and swine solid (Cantrell et al., 2012) pyrolysed at 300 - 450°C had greater than pH 8, while for sewage sludge it was pH 5. When pyrolysed at 600°C, pH of biochar from sewage sludge (Hossain et al., 2011), dairy manure and sugar beet waste (Inyang et al., 2012) was 12, 10 and 9, respectively. The pH of sewage sludge is lower at low pyrolysis temperatures and higher at 600°C, than other feedstocks.

Table 2. 4: Summary of proximate analysis and surface area of biochars from various manure and sewage sludge-derived feedstocks

Feedstock	Pyrolysis Temp.	Characteristics					Reference
		Yield (%)	Volatile matter (%)	Ash content (%)	Fixed C (%)	Surface area (m ² g ⁻¹)	
Chicken litter	620	43 - 49	16	53.2	30.8	-	Ro et al., (2010)
Poultry litter	350	54.3	42.3	30.7	27.0	3.93	Cantrell et al., (2012)
	700	36.7	18.3	46.2	35.5	50.9	
Swine solid	350	62.3	49.8	32.5	17.7	0.9	
	700	36.4	13.4	52.9	33.8	4.1	
Dairy manure	350	54.9	53.5	24.2	23.2	1.64	
	700	35.0	27.7	39.5	34.7	186.5	
Poultry litter	350	72	36.7	35.9	-	1.10	Novak et al., (2009)
	700	44	14.1	52.4	-	9.0	
Human manure	300	51.9	60.5	26.3	13.2	-	Liu et al., (2014)
	400	44.7	53.1	31.3	15.6	-	
	500	35.1	31.8	45.5	22.7	-	
	600	31.2	11.8	58.8	29.4	-	
	700	30.6	6.3	62.5	31.2	-	
Sewage sludge	300	72.3	33.8	52.8	9.1	-	Hossain et al., (2011)
	400	63.7	25.7	63.3	6.8	-	
	500	57.9	20.7	68.2	7.6	-	
	700	52.4	15.8	72.8	8.3	-	
Municipal wastewater sludge	300	81.6	-	-	-	7.90	Zhang et al., (2013)
	400	76.1	-	-	-	23.72	
	500	73.6	-	-	-	20.12	
	600	71.3	-	-	-	16.00	

“-“ indicates that the value was not indicated in the article.

Table 2. 5: Summary of composition of selected heavy metals and phosphorus in different biochar types from different feedstocks

Feedstock	Pyrolysis Temp.	Metal composition (mg kg ⁻¹)				Phosphorus (%)	pH	Reference
		Cd	Zn	Cu	Cr			
Digested sugar beet	600	-	10,800	100	100	0.54	9.0	Inyang et al. (2012)
Pine-wood sawmill	450	-	-	-	-	-	9.4	Sika and Hardie (2014)
Dairy waste	600	-	200	100	-	0.36	10.0	Inyang et al. (2012)
Dairy manure	350	0.18	361	99.0	6.58	1.0	9.2	Cantrell et al. (2012)
	700	BD	423	1,630	10.1	1.7	9.9	
Poultry Litter	350	0.25	712	213	5.00	2.1	8.7	
	700	0.11	1,010	310	6.86	3.1	10.3	
Swine solids	350	0.57	3,181	1,538	24.8	4.0	8.4	
	700	0.23	4,981	2,446	36.5	5.9	9.5	
Sewage sludge	300	-	1,675	1,150		-	5.3	Hossain et al. (2011)
	400	-	1,825	1,125		-	4.9	
	500	-	2,100	1,325		-	7.3	
	600	-	2,175	1,500		-	12.0	
Sewage sludge	300	-	1,480	385	157	-	-	Zhang et al. (2013)
	400	-	1,600	415	214	-	-	
	500	-	1,640	431	229	-	-	
	600	-	1,740	449	183	-	-	
Sewage sludge	300	-	-	-	-	3.9	-	Yuan et al. (2016)
	400	-	-	-	-	4.3	-	
	500	-	-	-	-	4.5	-	
	600	-	-	-	-	4.5	-	
	700	-	-	-	-	4.9	-	

“-“ indicates that the value was not indicated in the article. BD = below detection.

2.6 Organic material that can be pyrolysed to biochar in South Africa

Biochar characteristics, which are dependent on pyrolysis conditions and feedstock, are essential for its effectiveness for immobilising heavy metals in effluents and amended soils. The most common organic wastes that could be used for biochar production in South Africa are human faecal wastes and bark and wood wastes from the forestry industry. These feedstocks are commonly produced and are obtainable in large quantities in South Africa. Although some of these wastes have been used to produce biochar in the literature, the findings from literature shows variations in biochar characteristics within an individual feedstock, possibly due variations in feedstock characteristics from different regions. Moreover, there are limited studies on sewage sludge while no studies could be accessed in the literature on biochar from latrine waste, which is a major waste in southern Africa.

2.6.1 Human faecal waste

Austin (2002) and Mnkeni and Austin (2009) reported that an average person produces 7.5 - 15 kg of dry matter faeces per annum. Knowles et al. (2011) reported that at least 27 kg of dried biosolids per person per year is produced in countries with sewer treatment plants. The chemical composition of human faeces from different regions differs owing to standards of living, lifestyle and eating customs (Mnkeni and Austin, 2009). Table 2.6 shows that chemical composition of sewage sludge differs from country to country. The differences in chemical composition between sewage sludge from South Africa and other regions suggest that the characteristics of biochar could also differ. Sewage sludge in South Africa may be transformed through pyrolysis as a waste management strategy (Paz-Ferreiro et al., 2012; Mendez et al., 2012; Hossain et al., 2011) and produce biochar that can be used for immobilisation of pollutants from effluents and amended soils. Sewage sludge biochar is more stable in soil system than its raw feedstock due to its recalcitrance (Gasco et al., 2012), and increase nutrient availability and soil condition (Hossain et al., 2010) and improve soil quality (Paz-ferreiro et al., 2012).

Biochar produced from sewage sludge has the ability to increase EC, pH and N and P contents in the soil system (Hossain et al., 2010). Again, it is able to decrease the

bioavailability of metals found in it (Mendez et al., 2012; Hossain et al., 2010). The properties of biochar and its effects are dependent on the chemical composition of the feedstock as well as pyrolysis treatment. In addition to differences due to feeding habits, processing and storage may also affect the chemical composition of human waste from the same region with effects on characteristics of biochar produced. In addition to sewage sludge production, other human waste comes from pit latrines and urine-diversion toilets in South Africa.

Fidjeland et al. (2013) and Mihelcic et al. (2011) reported that improved sanitation facilities are common in parts of sub-Saharan countries, where sewer systems do not exist. Various types of latrines, including urine-diversion toilets and ventilated-improved pit latrines, have been installed as an appropriate technology to concentrate and accommodate human excreta in South Africa (Austin, 2002; Mihelcic et al., 2011; Nikiema et al., 2013). These systems are emptied periodically with cycles of a few years. While sewage sludge and latrine wastes are both human solid wastes, their differences in management could result in differences in characteristics which could affect the characteristics of the biochar and their ability to immobilize metals from solution and in the soil, with effects on leaching and uptake by plants. On the other hand, pine-bark biochar could have different characteristics from those of human faecal waste and differ in the immobilization of heavy metals.

2.6.2 Pine-bark

South Africa produced pine (*Pinus radiata*) on about 57,000 ha in 2008, mainly for saw logs, veneer logs, posts and poles (Mead, 2013). Pine-bark contains high levels of phenolic compounds such as catechin, epicatechin, taxifolin and phenolic acids (Aspe and Fernandez, 2011; Yesil-Celiktas et al., 2009) and is highly acidic, making direct application to the soil for C sequestration problematic (Aspe and Fernandez, 2011). Pyrolysis of this product could increase its pH, surface properties and aromatic character, making it possible to sequester C and neutralise soil pH when added to soil, while its surface area and activity could make it a sorbent for immobilising heavy metals.

Table 2. 6: Chemical composition of sewage sludge of different countries

Properties	China ^a	India ^b	New Zealand ^c	Spain ^d	USA ^e	South Africa ^f
pH	6.32	7.0	4.1	8.6	-	7*
Organic Matter (%)	37.7	-	48.2	43.4	51.6	59.2
Total N (%)	5.12	1.73	2.7	2.5	4	3.48
Total P (%)	0.55	0.072	0.47	1.06	1	1.55
Ca (%)	-	-	0.98	-	2	4.45
Potassium (%)	-	-	-	0.2	0.2	0.35
Copper mg (kg ⁻¹)	15.9	318	561	174	740	388
Cadmium (mg kg ⁻¹)	1.6	155	2.8	1.0	7	10**
Zinc (mg kg ⁻¹)	56.2	785	878	445	1200	103
Manganese (mg kg ⁻¹)	153	186	-	-	-	520
(a) Yan-Chao et al. (2014)				(e) Berthouex and Brown (2013)		
(b) Singh and Agrawal (2010)				(f) Turner, Wood and Meyer (1991)		
(c) Taghizadeh-Toosi et al. (2011)				(f*) Linder and Lundehn (2002)		
(d) Martinez et al. (2002)				(f**) Snyman et al. (2004)		

“-“ indicates that the value was not indicated in the article.

2.7 Conclusions

Biochar used as sorbent for heavy metals is mainly derived from forestry wastes, crop residues and animal manures, while the use of biochar from sewage sludge is limited, and that from latrine waste is not reported at all in the literature.

Biochar from manures and sewage sludge appears to sorb higher quantities of metals than plant waste-derived biochar, but this effect differs between single and multiple metal solutions, for some metals. Ash content, pH, surface area and surface functional groups are important characteristics of biochar as a sorbent for heavy metals. From this review, decline in biochar yield and volatile matter showed the following trend: plant material > animal manure > sewage sludge, while ash content followed the reverse trend. At high pyrolysis temperature (700°C), plant waste biochar show higher surface area than those from animal manure and sewage sludge, while in the 300 - 400°C pyrolysis temperature range, sewage sludge biochar had higher surface area than animal manure biochar.

Sewage sludge biochar pH appears to be lower at low pyrolysis temperature and higher at high pyrolysis temperatures than those from plant waste and animal manure.

Similarly to ash content, heavy metal and phosphorus concentrations in biochar increased with pyrolysis temperature, and appear to be in the following order of feedstocks: swine solid > sewage sludge > poultry litter > dairy manure. No heavy metals were reported in plant-derived biochar.

Characteristics of biochar from latrine waste have not been reported in the literature. Biochar from this feedstock has not been reported in this region. Latrine waste has commonly been used in palletisation process by the latrine dehydration and pasteurization protocol. While the trends of different biochar characteristics between sewage sludge, animal manure and plant waste biochar types appear to be clear, they are based on different studies, with different pyrolysis and sorption conditions, including retention times for production of the biochar types. Sewage sludge, latrine waste and pine-bark are major organic wastes that can be used for biochar production South Africa. Studies are required to determine comparative characteristics, sorption properties and immobilisation, in soil, of biochar from these organic wastes, under similar conditions.

CHAPTER 3: BIOCHAR TYPES FROM LATRINE WASTE AND SEWAGE SLUDGE DIFFER IN PHYSICOCHEMICAL PROPERTIES AND CADMIUM ADSORPTION

(Published in the American Journal of Applied Sciences)

3.1 Introduction

The global generation of human faecal waste has increased over the past decades exacerbating the challenges of waste disposal (Seo *et al.*, 2004; Al-Khatib *et al.*, 2010). Cities in Southern African produce large quantities of human faecal wastes from wastewater treatment plants (sewage sludge) and pit latrines. Zuma *et al.* (2015) reported that 31.3% of households in South Africa depend on pit latrines, and 12.5% use the ventilated improved pit latrines (VIP), for their sanitation needs. The processes of filling of the pit with faecal matter (and other wastes), water transfer and biological transformations, over a 5-year cycle (before emptying) (Zuma *et al.*, 2015) influence the chemical composition of the latrine waste. Communities in the cities largely depend on the sewer systems, which treat wastewater and produce sewage sludge, through the anaerobic digestion and separation of the solid from the liquid (Snyman and Herselman, 2009). Exploitation of these organic wastes, particularly for production of resources like biochar, is essential for minimizing environmental pollution with heavy metals, and other benefits (Gerente *et al.*, 2007). Differences in handling of latrine wastes and sewage sludge could result in variation in their characteristics (Tesfamariam *et al.*, 2009), and the resultant biochar. Biochar from organic wastes has shown potential for removal of heavy metals from wastewater (Namgay *et al.*, 2010; Major, 2011; Kim *et al.*, 2013; Mohan *et al.*, 2014; Coumar *et al.*, 2016). Heavy metals, a group of elements with at least five times the density of water, are challenging environmental pollutants in places with elevated anthropogenic pressure (di Toppi and Gabbrielli, 1999). The metals enter the soil through pathways including agricultural, mining and other industrial activities (Coumar *et al.*, 2016; Kabata-Pendias, 2000; Prasad, 1995). Production of biochar

from latrine waste and sewage sludge could have potential uses in heavy metal removal from wastewater. Pyrolysis of these faecal wastes to biochar could recover carbon and nutrients (Hossain et al., 2011; Paz-Ferreiro et al., 2012; Mendez et al., 2012), and result in a product that has potential as a sorbent for heavy metals.

The effectiveness of biochar as a sorbent depends on its characteristics owing to the properties of the feedstock (Maraseni, 2010; Mitchell et al., 2013) and pyrolysis conditions (Trakal et al., 2014; Wan et al., 2014, Kuppusamy et al., 2016; Bogusz et al., 2015). Differences in chemical composition of faecal wastes, as affected by diets (Mihelcic et al., 2011) and management, could influence characteristics of biochar produced from sewage sludge and latrine faecal wastes. Pyrolysis of these marginal organic materials to biochar could maximize their benefits (van Zwieten et al., 2010; Buss et al., 2016). The objective of this study was to determine effects of pyrolysis temperature on yield, characteristics and cadmium sorption capacities of biochar from latrine wastes relative to sewage sludge.

3.2 Materials and methods

3.2.1 Biochar feedstock

Latrine faecal wastes and domestic sewage sludge were used for producing biochar in this study. The latrine waste was obtained by manually emptying of ventilated and improved pit latrine (VIP) toilets in the eThekweni Municipality, South Africa. Due to non-separation of urine from faeces, the waste appeared like pseudo-plastic fluid. The faecal wastes were pelletized by the latrine dehydration and pasteurization (Latrine waste) process at 200°C for eight minutes. The sewage sludge was collected from drying beds at Howick Wastewater Treatment Plant, 15 km north-west of Pietermaritzburg. The plant produces domestic sewage sludge with minimal industrial contamination. The latrine waste had lower C, N, Na and higher Ca, K, C: N and CEC than sewage sludge (Table 3.1).

Table 3. 1: Chemical properties (means \pm standard error) of sewage sludge and latrine waste pellets used for pyrolysis

Property	Latrine waste	Sewage sludge
Total carbon (%)	9.29 \pm 0.17	28.6 \pm 0.45
Total nitrogen (%)	0.86 \pm 0.01	4.97 \pm 0.87
C:N	10.8	5.8
Ca (cmol+ kg ⁻¹)	32.2 \pm 0.93	20.8 \pm 0.74
Mg (cmol+ kg ⁻¹)	24.2 \pm 0.54	25.1 \pm 1.11
K (cmol+ kg ⁻¹)	4.12 \pm 0.02	2.68 \pm 0.08
Na (cmol+ kg ⁻¹)	0.69 \pm 0.02	14.7 \pm 0.59

3.2.2 Biochar production

The feedstocks were dried at 70°C for 24 h and milled to <5mm and slowly pyrolysed in 500 ml crucibles in a muffle furnace, equipped to reduce rapid oxidation and auto-ignition (Yuan et al., 2011; Enders et al., 2012). The furnace temperature was raised to set levels of 350, 550 and 650°C at the rate of 10°C min⁻¹, and pyrolysed for 2 h (Bamminger et al., 2014), in triplicate. The biochar was weighed to determine yield before characterization (Herath et al., 2013).

3.2.3 Volatile matter, ash content and fixed C

Volatile matter and ash content were determined using the proximate analyses following the reapproved American Society for Testing and Materials (ASTM) D1762 – 84 protocol (Wu et al., 2012). The pulverized samples were oven dried at 105°C for 2 h to determine moisture content. The biochar was subjected to 950°C furnace condition for six minutes and weight loss was taken as volatile matter, expressed as

a percentage on a dry weight basis. Ash was determined after combustion at 750°C for six hours. Fixed C was calculated by subtraction of volatile matter (%) and ash (%) from 100% (Liu et al., 2014).

3.2.4 Elemental composition and physicochemical properties

Total C and N were analyzed by dry combustion using LECO Trumac CNS analyzer (LECO Corporation, 2012). Furthermore, CHNS elemental analyzer was used to determine total H. The pH of biochar was determined in H₂O and KCl at a solid: solution ratio of 1:20 w/v ratio because of low bulk density of biochar (Cheng and Lehmann, 2009). The concentrations of exchangeable basic cations were extracted with 1M NH₄OAc at pH 7. The air-dried biochar (5.0 g) was suspended in 100ml of 1M ammonium acetate (NH₄OAc), and the mixtures were mechanically shaken at 180 rpm for an hour then filtered. The filtrate was analyzed for basic cations, using flame photometry (K⁺ and Na⁺) and atomic absorption spectrometry (Ca²⁺ and Mg²⁺). Cation exchange capacity (CEC) was determined as the concentration of NH₄⁺ retained after leaching with several portions of ethanol (Ross and Ketterings, 2011).

3.2.5 Functional groups, surface area and porosity

Chemical functional groups of the biochar were determined using the Fourier Transform Infrared (FTIR) spectroscopy (Coates, 2000). The FTIR transmission spectra were recorded on a PerkinElmer FT-IR at the wave numbers ranging from 550 to 4000 cm⁻¹ (Wu et al., 2012). Chemical functional groups were then assigned to the wave numbers from the FTIR spectra. Brunauer–Emmett–Teller (BET) surface area and pore volume and size were measured by nitrogen gas sorption analysis at 77K bath temperature using Micromeritics Gemini BET Surface Area Analyser, following the method used by Brewer et al. (2011).

3.2.6 Batch Cd sorption studies

The capacity of the biochar to sorb cadmium (Cd) was evaluated using a batch sorption study. The batch tests were replicated three times and blanks were run concurrently (Mohan et al., 2007). A stock solution of 1000 mg Cd L⁻¹ was prepared by dissolution of analytical grade of the metal in a 0.01 M CaCl₂ as a background electrolyte. The solution was diluted to 5, 10, 15, 20, and 25 mg Cd L⁻¹ solutions with 0.01 M CaCl₂. The 0.01 M CaCl₂ solution was used as the 0 mg L⁻¹ concentration. The different concentrations were used in order to accomplish plotting of the isotherms; amount adsorbed to be plotted against solution equilibrium concentration (Ali, 2010). The Cd solutions (25 ml) were added to centrifuge tubes containing 2.5 g biochar samples. The suspensions were shaken at 180 r min⁻¹ at constant temperature (25°C) for 24 h (Khodaverdiloo and Samadi, 2011) on a reciprocating shaker. The suspensions were centrifuged at 9440*g for 10 min and the supernatants filtered through Whatman no. 42 filter paper (Khodaverdiloo and Samadi, 2011). A Fast Sequential Atomic Absorption Spectrometer (Model AA280FS) was used to measure Cd concentration in the supernatant. The pH of the supernatant was also measured. Amount of Cd sorbed (S) was calculated as the difference between amount added and amount in the equilibrium solution, using Equation 1 (Desta, 2013):

$$S = \frac{(C_0 - C_e) * V}{W} \quad \text{Equation 3.1}$$

Where **S** is the amount of Cd sorbed (mg kg⁻¹), C₀ and C_e are the initial and equilibrium solution Cd concentrations (mgL⁻¹), V is the solution volume (L), and W is the adsorbent weight (kg).

3.2.7 Data analysis

All biochar characteristics were subjected to two-way analysis of variance (ANOVA) to show effects of pyrolysis temperature and feedstock type using Stata/IC 13.1 Edition (Stata, 1985 – 2013). Adsorption data were fitted to a Langmuir isotherm and sorption capacities were estimated (Kumar et al., 2011). Step-wise regression

analysis was used to identify the best fit model to explain Cd sorption data by removing certain variables based on the t-statistics (Gray et al., 1999).

3.3 Results

3.3.1 Yield, volatile matter, fixed carbon and ash content of faecal biochar

Biochar from latrine waste had higher yields than from sewage sludge and the yields decreased with increase in pyrolysis temperature (Figure 3.1). Increasing pyrolysis temperature from 350°C to 550°C decreased biochar yield by 6.7% (83.4% to 76.7%) for latrine waste, and by 32.9% (74.3 to 41.4%) for sewage sludge. The least yield of latrine waste biochar (650°C) was similar to the highest for sewage sludge (350°C).

Volatile matter was higher in biochar from sewage sludge than latrine waste and the composition decreased with increase in pyrolysis temperature (Figure 3.1). There was no significant difference in volatile matter on sewage sludge biochar at 550°C and latrine waste biochar at 350°C.

Sewage sludge biochar had higher fixed C than from latrine waste (Figure 3.1). Increasing pyrolysis temperature from 350 and 550°C increased fixed C in sewage sludge biochar and while the fixed C decreased for latrine waste biochar. There were no differences in fixed C between 550 and 650°C for both feedstocks.

3.3.2 Total carbon, nitrogen and hydrogen composition of biochar

Biochar from latrine waste had lower total C and N than sewage sludge biochar and the composition decreased with increase in pyrolysis temperature (Table 3.2). The trends were the opposite of that of ash. The C: N ratio was higher for latrine waste biochar than sewage sludge, and generally increased with increase in pyrolysis temperature. The increase in pyrolysis temperature from 350 to 550°C resulted in decrease in H content in biochar from both feedstocks (Table 3.2). The H:C ratios followed the same trend as that of H composition of the biochar. The decrease in H led to a decrease in H:C molar ratio, an index of biochar aromaticity.

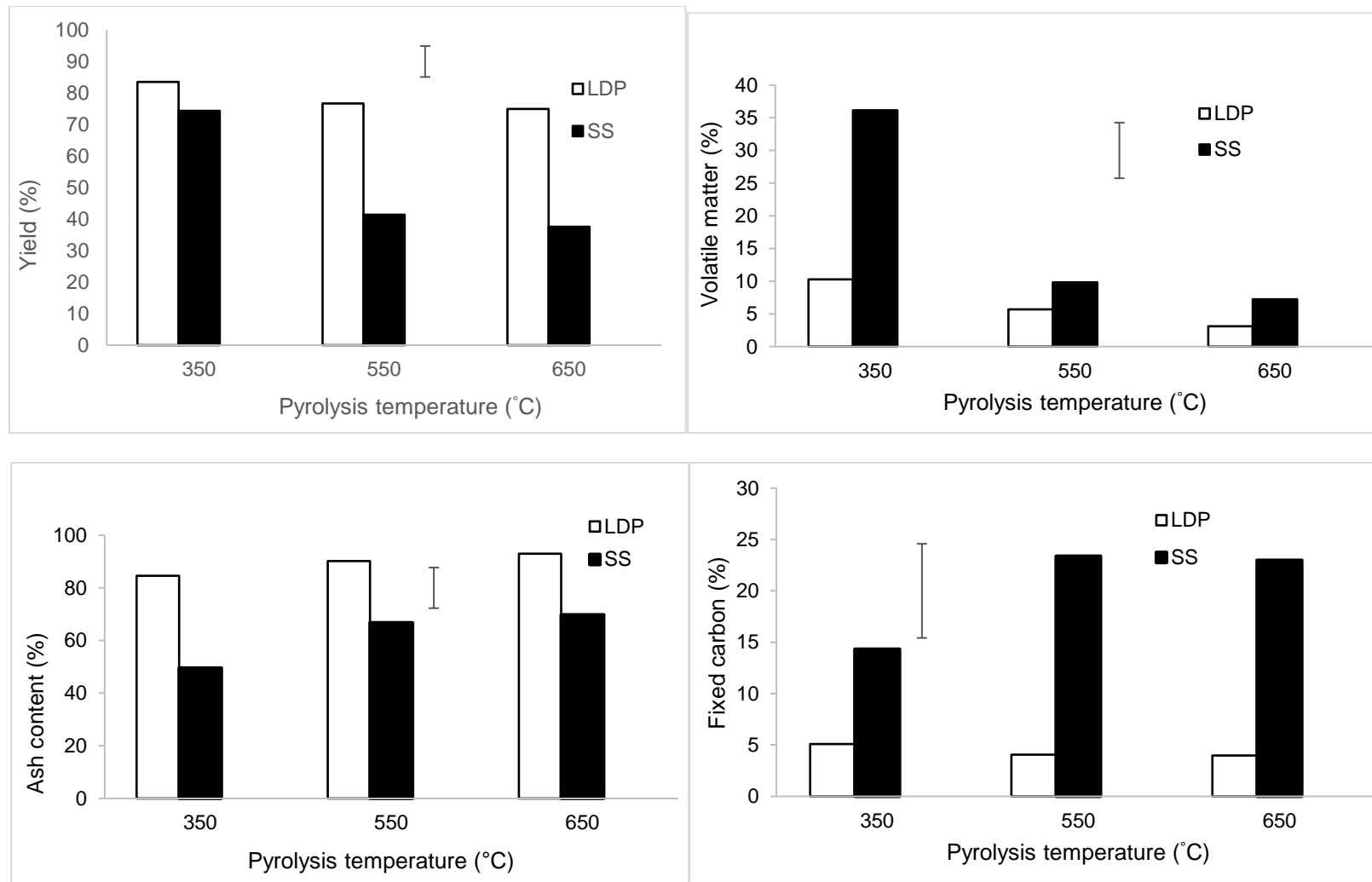


Figure 3. 1: Yield, volatile matter, ash content and fixed carbon of biochar from latrine waste (LDP) and sewage sludge (SS) at different pyrolysis temperatures. Error bars indicate statistical significant difference

Table 3. 2: Carbon, nitrogen and hydrogen composition of the faecal biochar types

Feedstock	Temperature (°C)	C (%)	N (%)	H (%)	C/N	H/C
Latrine waste	350	11.14d	1.04c	1.01b	11:1	1.1
	550	8.73ed	0.71dc	0.36c	12:1	0.3
	650	6.45e	0.44d	0.35c	15:1	0.4
Sewage sludge	350	31.19a	5.45a	2.64a	6:1	1.0
	550	17.27c	2.64b	1.02b	7:1	0.7
	650	20.85b	2.77b	0.71cb	8:1	0.3

Means followed by the same letter in each column are not significantly different at $p < 0.05$.

3.3.3 pH, exchangeable bases and cation exchange capacity

Biochar pH increased with increase in pyrolysis temperature (Table 3.3). At 350°C latrine waste biochar had higher pH than sewage sludge, while at 550 and 650°C sewage sludge biochar had higher pH than latrine waste. Exchangeable Ca was higher in latrine waste biochar than from sewage sludge, with no effects of pyrolysis temperature. Exchangeable K was lower in latrine waste than sewage sludge biochar. The composition decreased in sewage sludge biochar by raising pyrolysis temperature from 350 to 550°C and increased in latrine waste biochar from 550 to 650°C. Exchangeable Mg was lower in latrine waste biochar than sewage sludge at 350°C.

3.3.4 Chemical functional groups of faecal biochar

The chemical functional groups of biochar are shown in Table 3.4. The C-H bending of aromatic C, aromatic P-O-C ($1240\text{-}1190\text{ cm}^{-1}$) and O-H of carboxylic acid groups were present in all biochar irrespective of feedstock and pyrolysis temperature. The aldehyde C=O group occurred only in biochar pyrolysed at 350°C for both feedstocks. Latrine waste biochar lacked the C=C bending of aromatic C and the aromatic carbon C=O functional groups, which were present in sewage sludge biochar. Latrine waste biochar had amide N-H (except 650°C) and secondary amine N-H groups, which were absent in sewage sludge biochar. All biochar had the ring stretching of aromatic C (C=C-C) except the sewage sludge biochar pyrolysed at 350°C. Aromatic phosphate functional group ($995\text{-}850\text{ cm}^{-1}$) was only present in latrine waste biochar pyrolysed at 350 and 550°C. On the other hand, the latrine waste biochar produced at 650°C was the only one with the phenol O-H tertiary alcohol functional group ($1410\text{-}1310\text{ cm}^{-1}$). The C=O stretching of aldehyde on latrine waste biochar diminished with increase in pyrolysis temperature.

Table 3. 3: pH, exchangeable bases and cation exchange capacity of biochar types

Elements	Latrine waste			Sewage sludge		
	350°C	550°C	650°C	350°C	550°C	650°C
pH (H ₂ O)	6.94b	7.02bc	7.14cd	5.89e	7.27d	7.56 a
pH (KCl)	6.93d	7.03d	7.17c	6.0 5e	7.47b	7.86 a
Exchangeable Ca (cmol+ kg ⁻¹)	9.74b	17.3a	18.8a	5.47c	2.78c	3.19 c
Exchangeable Mg (cmol+ kg ⁻¹)	3.08b	4.06ab	4.32ab	4.88a	3.44ab	4.65 a
Exchangeable K (cmol+ kg ⁻¹)	0.94d	1.04cd	0.58e	3.30a	1.25cb	1.45 b
Exchangeable Na (cmol+ kg ⁻¹)	0.90c	1.40b	0.98c	2.01a	0.44d	1.02 c
Cation exchange capacity (cmol+ kg ⁻¹)	5.09a	4.91a	5.65a	4.17ab	2.31c	2.40 bc

Means followed by the same letter in each row are not significantly different at $p < 0.05$.

Table 3. 4: FTIR spectra of faecal biochars produced at different pyrolysis temperatures

Actual group frequency, wave number cm^{-1}	Functional group	Biochars					
		Latrine waste			Sewage sludge		
		350°C	550°C	650°C	350°C	550°C	650°C
*3700 – 3500	N-H stretching of amide	3694.07	3691.69				
3570 – 3200	O-H stretching of phenol				3338.16		
*3000 – 2500	O-H stretching of carboxylic acid	2642.94	2645.18	2646.13	2924.7	2644.1	2795.73
*1740 – 1690	C=O stretching of aldehyde	1714.77			1706.19		
*1700 – 1500	C=C bending of aromatic carbon				1559.47	1559.89	1560.98
1650 – 1550	N-H secondary amine	1559.16	1561.18	1561.22			
1510 – 1450	C=C-C ring stretching of aromatic C	1497.09	1497.09	1497.04		1497.14	1496.98
1490 – 1410	Carbonate ions				1446.79		
1410 – 1310	O-H bending of phenol (tertiary alcohol)			1356.09			
1240 – 1190	P-O-C stretching of aromatic phosphates	1219.90	1219.86	1219.87	1219.85	1220	1220.03
1100 – 1000	Phosphate ions						1068.05
1050 – 990	Aliphatic phosphate	1007.95	1009.67	1046.97	1047.04	1048.24	
995 – 850	Aromatic phosphates	913.16	914.83				
860 – 680	C-H bending of aromatic C	772.61	773.06	772.94	772.94	772.52	772.85

Encyclopaedia of Analytical Chemistry (Coates, 2000) *WebSpectra (Merlic, 1997).

3.3.5 Surface area, pore volume and pore size

Latrine waste biochar had higher surface area and pore volume than those from sewage sludge (Figure 3.2). Surface area and pore volume increased, whereas pore size decreased, with increase in pyrolysis temperature. There was greater change in surface area, pore volume and pore size as a result of increasing pyrolysis temperature from 350 to 550°C than from 550 to 650°C.

3.3.6 Cadmium sorption on faecal biochar

The Cd sorption data fitted the Langmuir isotherms are on Figure 3.3a and b. Cadmium sorption capacities and constants relating to bonding energy (b) of different biochar are on Table 3.5. The R^2 were > 0.900 . Cadmium sorption on both latrine waste and sewage sludge decreased with increase in pyrolysis temperature, except that sorption on latrine waste biochar at 550°C was higher than that on 350°C. The constants relating to bonding energy were higher on latrine waste ($\geq 40 \text{ L kg}^{-1}$) than sewage sludge ($< 1.2 \text{ L kg}^{-1}$).

3.3.7 Relationships of biochar characteristics and cadmium sorption

Step-wise regression analysis (Table 3.6) showed that Cd sorption capacity could be explained ($p < 0.05$) by a combination of ash and total P (**$S_{\text{max}} = 1.960 \text{ ash} - 9.028 \text{ total P} + 255.696$**), and of ash and pH (**$S_{\text{max}} = 4.177 \text{ Ash} - 97.429 \text{ pH} + 525.562$**). Although there appears to be relationships between Cd sorption capacity and ash, surface area, and CEC, only ash, total P and pH had significant effects. Omission of ash led to insignificant effect with low correlation coefficient and $p > 0.05$.

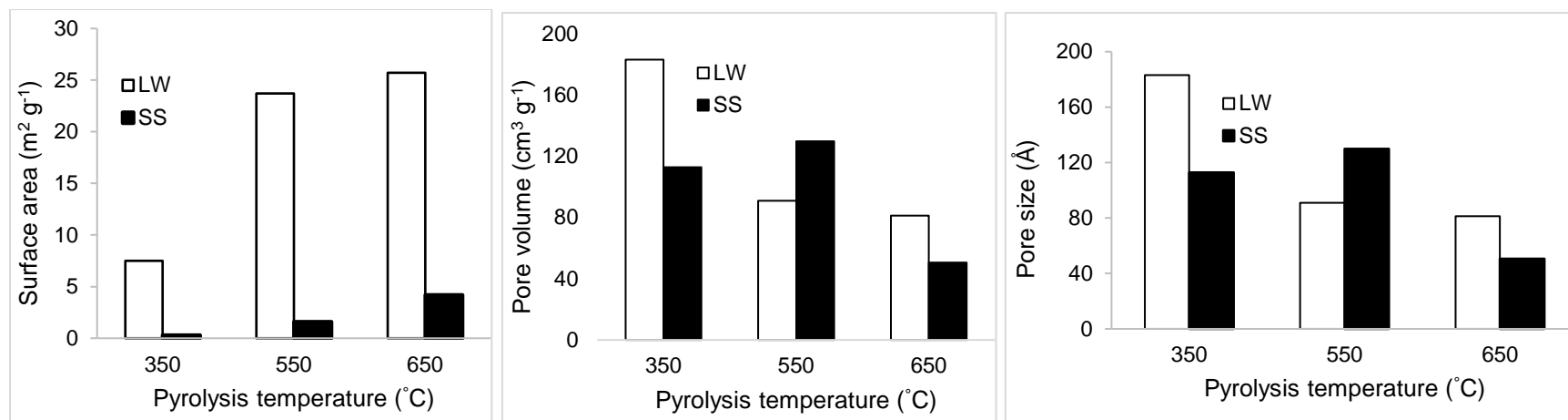


Figure 3. 2: Surface areas, pore volumes and pore sizes of biochar from latrine waste (LW) and sewage sludge (SS) at different pyrolysis temperatures

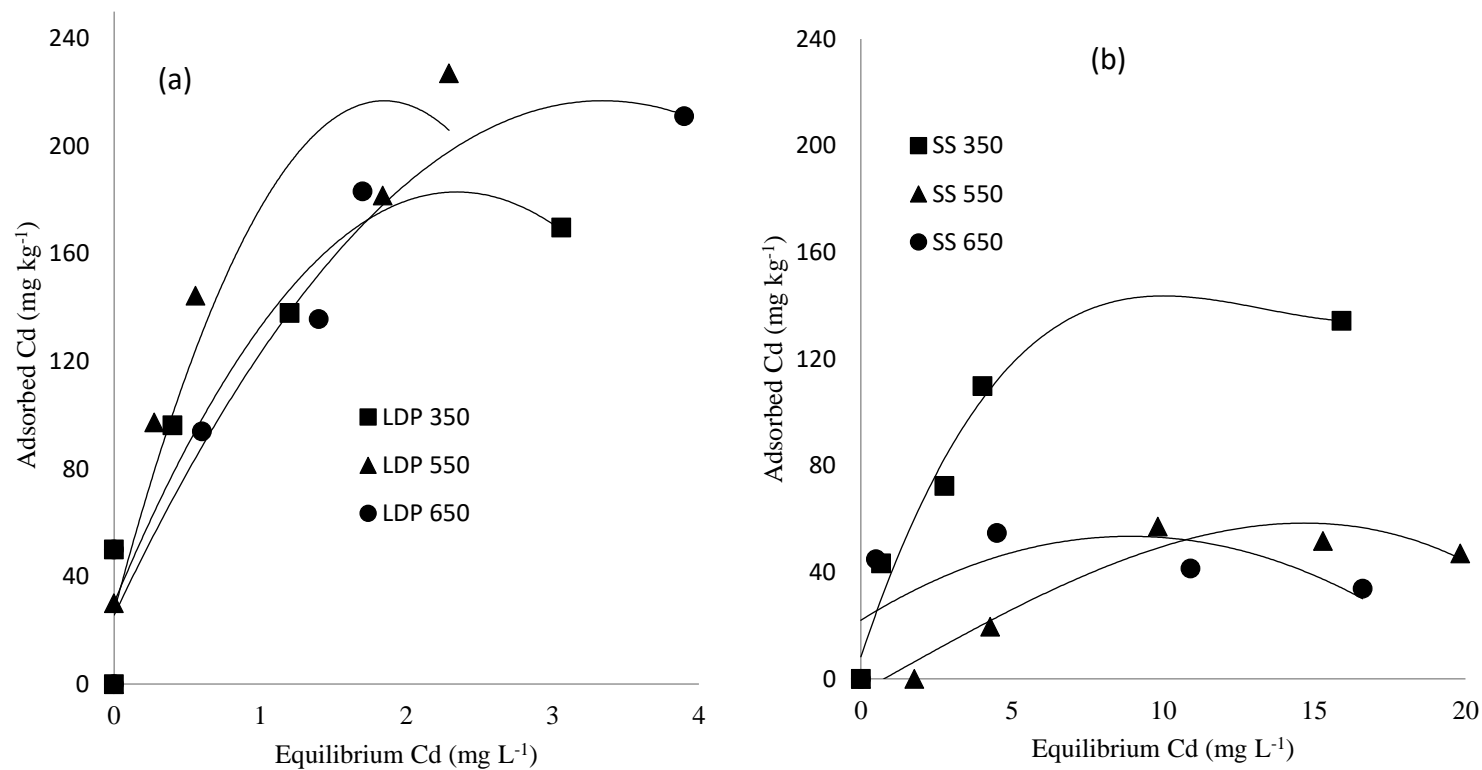


Figure 3. 3: Adsorption isotherms of cadmium on different types of biochar from (a) latrine waste (LDP) and (b) sewage sludge (SS). LDP350, LDP550 and LDP650 are different types of biochar from latrine waste produced at 350, 550 and 650°C, respectively.

Table 3. 5: Langmuir adsorption parameters of cadmium on the different biochar types

Feedstock	Pyrolysis Temperature (°C)	Smax (mg kg ⁻¹ Cd)	b (L kg ⁻¹ Cd)	R ²
Latrine waste	350	200	50.0	0.98
	550	250	40.0	0.96
	650	167	60.0	0.90
Sewage Sludge	350	143	0.78	0.98
	550	55.6	1.13	0.97
	650	35.7	-1.56	0.98

Table 3. 6: Step-wise regression analysis to identify the most influential parameter(s) on cadmium adsorption

Parameter	Coefficient	P > t	P as a whole
Ash %	2.416	0.251	0.161
Total P (g kg ⁻¹)	-7.607	0.201	
Total Al (g kg ⁻¹)	-1.591	0.669	
Constant (α)	211.184	0.325	
Ash %	1.960	0.155	0.044
Total P (g kg ⁻¹)	-9.028	0.035	
Constant (α)	255.696	0.119	
Ash %	3.995	0.101	0.169
Total Al (g kg ⁻¹)	-5.872	0.152	
Constant (α)	-44.703	0.740	
Total P (g kg ⁻¹)	-11.204	0.073	0.127
Total Al (g kg ⁻¹)	1.531	0.659	
Constant (α)	436.51	0.023	
Ash %	4.177	0.018	0.025
pH _{KCl}	-97.429	0.019	
Constant (α)	525.562	0.036	

3.4 Discussion

The loss of organic C, associated with thermal degradation of lignocellulosic biomass and dehydration of organic compounds, explains the decrease in biochar yield with pyrolysis temperature (Liu et al., 2014). Thermal degradation of sewage sludge (higher total C) explains greater decline in yield and increase in total elemental composition than those from latrine waste with increasing pyrolysis temperatures. Sewage sludge biochar yields were lower than reported by Yuan et al. (2015), in the similar range reported by Hossain et al. (2011), and higher than reported by Agrafioti et al. (2013). Differences in composition of the sludge could explain the variation.

The decrease in yield and volatile matter with increase in pyrolysis temperature was in agreement with Yuan et al. (2011), Enders et al. (2012), Wu et al. (2012), Mitchell et al. (2013), Hmid et al. (2014) and Liu et al. (2014), for a variety of feedstocks. Degradation of organic material (loss of volatile solids) during long storage times in the latrine (Zuma et al., 2015) explained the higher ash content in latrine waste (85-93%) than sewage sludge (50-70%) biochar. The higher ash content in the two faecal wastes indicated lower organic C content when compared with other feedstocks in the literature (Liu et al., 2014). The increase in fixed C with pyrolysis temperature was in agreement with Yuan et al., (2011), Enders et al. (2012), Wu et al. (2012), Mitchell et al. (2013), Hmid et al. (2014) and Liu et al. (2014).

The H:C ratios in this study suggest that the biochar did not have significant aromaticity. Generally, the H:C of the biochar ranging 0.02 - 0.1 suggest condensed structure and more recalcitrant constituents (Kloss et al., 2012). Hmid et al. (2014) and van Zwieten et al. (2010) reported that biochar become more aromatic and carbonatious at high temperature due to a decline in H/C.

In latrine waste biochar, P content and pH did not change because the material was low in volatile solids, as a result of decomposition during storage. The increase in biochar pH with increase in pyrolysis temperature resulted into alkaline biochar (Wan et al., 2014). The lower CEC in sewage sludge biochar at 550 and 650°C, than the

other biochar types, in this study, was contrary to Mukherjee and Lal (2014), who reported that formation of phenolic groups might increase biochar CEC. In this study, phenolic groups were only present at 650°C for latrine waste and at 350°C for sewage sludge (Table 3.4). The high ash content and low C in faecal waste biochar could explain the difference, with literature. The higher CEC in latrine waste biochar could result in higher sorption of metals due to cation exchange (Inyang et al., 2016).

The occurrence of phenol O-H group ($3570\text{--}3200\text{ cm}^{-1}$) and carbonate ion ($1490\text{--}1410\text{ cm}^{-1}$) only on sewage sludge biochar pyrolysed at 350°C could be a result of formation of C=C-C groups from the phenol O-H and carbonate ion, due to increasing pyrolysis temperature. Reduction in biochar yield with increase in pyrolysis temperature is associated with dehydration of organic compounds such as those with hydroxyl, phenolic and carboxylic acid groups (Novak et al., 2009; Liu et al., 2014). The aliphatic phosphate functional group, which was present in all biochar except sewage sludge biochar pyrolysed at 650°C; the only one with phosphate ions, suggested that the functional group mineralized at high temperature.

The higher surface area and pore volume of latrine waste biochar suggested that these biochar could encourage more sorption than those from sewage sludge (Inyang et al., 2016). The increase in surface area and pore volume, and decrease in pore size, with increase in pyrolysis temperature, could be explained by escape of volatile components leaving voids (Ahmad et al., 2012; Downie et al., 2011). Lower volatile compounds and high ash content in latrine waste biochar, possibly because of C losses during storage, explains the higher porosity and surface area even at 350°C.

Latrine waste biochar had higher surface area than reported by Agrafioti et al. (2013) for sewage sludge. While latrine waste biochar had similar surface area than those reported by Yuan et al. (2015), sewage sludge biochar were lower. However, the pore volume in this study was lower, indicating less porous biochar. The increase in surface area and micro-porosity due to pyrolysis could enhance metal retention when used as adsorbents (Masto et al., 2013). The higher sorption capacity of latrine waste biochar than sewage sludge appeared related to the surface area. However, the

increase in surface area in latrine waste biochar was not correlated with Cd sorption. This was in agreement with Trakal et al. (2014), who reported that removal of Cd was least influenced by biochar morphology and specific surface area.

The fit of Langmuir model suggests that Cd sorption on the biochar is a monolayer process (Bogusz et al., 2015; Trakal et al., 2014). The greater sorption of Cd on latrine waste biochar than on sewage sludge biochar could be explained by the higher ash, CEC and surface area. The positive correlation of Cd sorption with ash content was in agreement with Xu and Chen (2014) and suggested that minerals in the ash dominated the sorption process. Calcium hydroxyapatite and calcium carbonates in bone biochar have been shown to promote ion exchange reactions of heavy metals (Inyang et al., 2016). The higher Ca than total P in latrine waste biochar indicate that Ca in the ash occurred mainly as carbonates, providing sorption sites for Cd (Xu and Chen, 2014). Phosphorus could have precipitated with Cd at pH 6.0 - 7.0, resulting in higher sorption than at higher pH. At higher pH, precipitates with Ca and Mg are formed, and P becomes less available to precipitate with Cd, lowering sorption. This effect would have been more important for sewage sludge, which had higher P and lower Cd sorption at higher pH (7.5-7.9). The decline in exchangeable Ca with pyrolysis temperature for sewage sludge supported this view. However, this effect could have been lower for latrine waste biochar, which had lower P.

3.5 Conclusions

Biochar from latrine faecal waste have higher yields, ash, Ca, Fe, surface area, porosity and cadmium sorption capacity, and lower fixed C, than those from sewage sludge. Increasing pyrolysis temperature increase surface area and porosity and decreases biochar yield, volatile matter and Cd sorption capacity. Surface functional groups on biochar differ between the faecal wastes and among pyrolysis temperatures. Ash, pH and P content are the most important parameters governing Cd sorption on faecal biochar. Further research is required on sorption of other heavy metals on these faecal biochar when compared with wood derived biochar.

CHAPTER 4: PYROLYSIS TEMPERATURE EFFECTS ON YIELD, PHYSICOCHEMICAL CHARACTERISTICS OF PINE-BARK BIOCHARS AND CADMIUM SORPTION

(Published in the Indian Journal of Environmental Protection)

4.1 Introduction

Forest products industries throughout the globe disposed of tonnes of wood and bark wastes, annually. This results in production of leachates from stockpiles of these wastes, characterized by tannic acids, oxygen-demanding materials, colour, odour and rendering ground-water non-potable (Sweet and Fetrow, 1975; Zimms and Berrett, 2004). The use of wood waste to manufacture secondary products such as particle boards and insulating bats has resulted in positive effects of reducing environmental pollution (Erlandsson and Sundquist, 2014; USDA, 2002). However, the volumes of such wastes from approximately 57 000 ha recorded in in 2008 are too large for this way of beneficial use and production of biochar could have potential uses in heavy metal removal from wastewater and as soil amendments in agriculture. The utilization of heavy metals such as Cd in various industries, and the discharge of the industrial wastes into the environment, lead to soil and water contamination (Bogusz et al., 2015), with potential ecological risks due to non-biodegradability and persistence of the metal (Cui et al., 2015). There has been a quest for inexpensive active carbon adsorbent substitutes for toxic metal ion removal from wastewater (Ali, 2010) and materials considered a wastes could be pyrolysed to maximize their benefits (Buss et al., 2016). The effective exploitation of organic waste materials, through biochar production, could yield low-cost sorbents of heavy metals (Gerente et al., 2007; Mohan et al., 2007), particularly when the world is faced with widespread environmental pollution. Biochar, a carbon-rich product of thermal degradation of organic biomass in an oxygen-limited environment (Lehmann and Joseph, 2009; Inyang et al., 2015), has been shown to be a suitable biosorbent for the removal of toxic metals from aqueous solutions and wastewater (Namgay et al., 2010; Major, 2011; Kim et al., 2013; Mohan et al., 2014; Coumar et al., 2016). The effectiveness

of biochar as a sorbent depends on its composition and surface characteristics owing to biochar preparation conditions and the properties of the feedstock (Li et al., 2014; Trakal et al., 2014; Bogusz et al., 2015; Kuppusamy et al., 2016).

Changes in pyrolysis temperature have been shown to affect thermal decomposition properties, C content, aromaticity (Hmid et al., 2014), surface functional groups (Wan et al., 2014), CEC (Hmid et al., 2014; Glaser et al., 2002), pore structure, size and distribution (Glaser et al., 2002; Mitchell et al., 2013;) of the carbonised material. Higher pyrolysis temperature has been shown to results in biochar with higher aromatic structure, pH and surface area, with increased Cd sorption capacity up to 13.24 mg g⁻¹ (Kim et al., 2012; Kim et al., 2013;).

Trakal et al. (2014) reported that biochars from nut shells, plum stones, wheat straws and grape stalks and husks can effectively remove Cd from aqueous solution. The ability oak-bark biochar to remove Cd from contaminated water was shown to be remarkable on the basis of metal adsorbed per unit surface area (Mohan et al., 2007). Bogusz et al (2015) reported that *Sida hermaphrodita* biochar had greater Cd adsorption efficiency than wheat-straw biochar owing to the effect of higher carbon and oxygen content. Pine husk biochar has been found to be an effective material capable of removing 99.9% of Cd from polluted environmental matrixes (Xu et al. 2013a, b). Where forestry products were used, the woody materials have been more commonly used as feedstocks for the production of biochar, particularly hardwoods, (Brewer et al., 2011). The prevalence of commercial pine forestry in Southern Africa produces large quantities of pine-bark.

Although pine waste has been used to make biochar, the woody part that excluded the bark (pine-bark) has been more commonly used (Singh et al., 2010; Brewer et al., 2011; Enders et al., 2012; Mitchell et al., 2013; Baronti et al., 2014). Pine-bark contains high levels of phenolic compounds such as catechin, epicatechin, taxifolin and phenolic acids (Yesil-Celiktas et al., 2009; Aspe and Fernandez, 2011) and is highly acidic, making direct soil application problematic (Aspe and Fernandez, 2011). While large quantities of pine-bark are used for the production of potting media through composting, a greater proportion of the waste present disposal challenges and end up being stockpiled on site (Zimms and Berrett, 2004; Erlandsson and

Sundquist, 2014). Pyrolysis of pine-bark could produce a biochar that has higher pH and fixed C and modified surface properties that will work as an effective sorbent for pollutants in wastewater and improve the quality of treated soil. There is little-to-no existing literature on the characteristics of biochar from pine-bark as affected by pyrolysis temperature. The objective of this study was to determine the effect of pyrolysis temperature on biochar yield, surface area, porosity, total elemental composition and cadmium sorption capacity of biochar from pine-bark. Another objective was to determine possible synergistic effects of pine-bark biochar and latrine waste/ sewage sludge biochar on Cd sorption.

4.2 Materials and methods

4.2.1 Biochar feedstock

Biochars used in this study were produced from pine (*Pinus radiata*) bark collected from a private forestry by-products and compost farm at Cramond, Pietermaritzburg. Pine-bark is the most common by-product from most forestry industries in South Africa. Pine-bark was selected based on its abundance and the challenges of their disposal. The chemical properties of the feedstock are presented in Table 4.1.

Table 4. 1: Chemical properties of pine-bark used for pyrolysis

Property	Pine-bark
Total carbon (%)	53.2 ± 0.10
Total nitrogen (%)	0.33± 0.01
C/N	163± 2.7
Ca (cmol+ kg ⁻¹)	0.70 ± 0.11
Mg (cmol+ kg ⁻¹)	1.86 ± 0.08
K (cmol+ kg ⁻¹)	1.76± 0.07
Na (cmol+ kg ⁻¹)	0.13± 0.01
CEC (cmol+ kg ⁻¹)	18.0± 0.16

4.2.2 Biochar production and analysis

The biochar was produced as detailed in Section 3.2.2. Biochar yield, volatile matter, ash content and fixed C were analysed as detailed in Section 3.2.3. Total elemental composition of the biochar was determined as described in Section 3.2.4. The surface functional groups, surface area and pore volume and sizes, of the biochar were determined as described in Section 3.2.5.

4.2.3 External morphology and surface characteristics

Scanning electron microscopy-energy dispersive x-ray spectroscopy was used to determine surface characteristics of the biochars. It was used to analyse the external morphology (texture and structure) and qualitative chemical composition of biochars. With SEM, the analyses involved a beam of electrons generated in a vacuum, which is collimated by electromagnetic condenser lenses and scanned across the sample surface by a coil. Secondary electrons were then made to fall on the surface of a photosensitive plate in a photomultiplier tube. Amplified electrons are sent to phosphorescent screen which provided magnified image of sample surface. Energy Dispersive X-ray Spectroscopy (EDS) was used to analyse the energy spectrum in order to determine abundance of specific available elements in a given sample.

4.2.4 Batch Cd sorption studies

The batch sorption study with pine-bark biochar and Cd solutions was done as detailed in Section 3.2.6. The sorption study was repeated with mixtures of increasing proportions of pine-bark and decreasing proportions of latrine waste or sewage sludge biochar (100:0, 75:25, 50:50, 25:75 and 0:100) to determine possible synergistic effects as a result of differences in sorption mechanisms, based on the higher sorption capacities of latrine waste and sewage sludge biochar. Three batch sorption studies were done with both pine-bark and latrine waste pyrolysed at (i) 350°C (ii) 650°C and (iii) pine-bark at 650 and sewage sludge pyrolysed at 350°C.

4.2.5 Statistical Analysis

Correlation and principal component analysis were used to identify the best fit model. Correlation analysis in Stata was done through list-wise deletion of some data by default (Gray et al., 1999).

4.3. Results

4.3.1 Biochar yield and composition of volatile matter, ash and fixed carbon

Biochar yield, volatile matter significantly decreased with pyrolysis temperature (Table 4.2). Increase in pyrolysis temperature from 350 to 550°C resulted in 19.20% decrease in volatile matter while a further increase from 550 to 650°C resulted in 9.47% decline. Ash content was not influenced by any increase in pyrolysis temperature. The average values ranged from 2.53 to 3.13%. Fixed C increased by 19.33% with increase in pyrolysis temperature from 350°C to 550°C and by 8.83% from 550°C to 650°C.

Table 4. 2: Yield and proximate analyses results of biochars from pine-bark

Pyrolysis temperature (°C)	Yield (%)	Volatiles (%)	Ash (%)	Fixed C (%)
350	57.62a	39.47a	2.63a	57.91c
550	40.14b	20.27b	2.53a	77.24b
650	36.56c	10.80c	3.13a	86.07a

Means followed by the same letter in each column are not significantly different at $p < 0.05$.

4.3.2 Total elemental composition of pine-bark biochar

Increase in pyrolysis temperature increased C content and C:N ($p < 0.05$), decreased H and H:C, and did not Affect N content of the biochar (Table 4.3). Biochar 350°C

had a higher average value of 3.31% which decreased to 1.64% as temperature increased to 650°C. The pattern biochar N showed a declining trend as pyrolysis temperature increased. The C:N increased from 100:1 to 201:1, while H:C decreased from 0.6:1 to 0.2:1. Concentrations of other elements were generally low (Table 4.4) and showed a general decline with increase in pyrolysis temperature. Table 4.5 shows the order of intensity of the detected elements. The order indicates that the concentration of Pb and Zn, Na and P and K and Al were least, median and highest in range respectively throughout all pyrolysis temperatures.

Table 4. 3: Carbon, N and H analyses of biochars from three pyrolysis temperatures

Temperature (°C)	C (%)	N (%)	H (%)	C/N	H/C
350	68.98c	0.69a	3.31a	100:1c	0.6:1a
550	83.08b	0.50a	2.62b	167:1b	0.4:1b
650	89.58a	0.44a	1.64c	201:1a	0.2:1c

Table 4. 4: Total elemental composition of pine-bark biochars

Elements	Temperature		
	350	550	650
Phosphorus (g kg ⁻¹)	0.45	0.32	0.31
Calcium (g kg ⁻¹)	1.2	0.6	0.7
Aluminium (g kg ⁻¹)	2.58	0.82	0.82
Magnesium (g kg ⁻¹)	0.28	0.06	0.05
Potassium (g kg ⁻¹)	1.78	1.29	0.94
Manganese (mg kg ⁻¹)	95	23	18.7
Iron (g kg ⁻¹)	0.51	0.49	0.61
Zinc (mg kg ⁻¹)	28	16	14.3
Lead (mg kg ⁻¹)	5.59	2.49	1.39

Table 4. 5: Order of intensity of total elements in pine-bark biochars

Temperature (°C)	Order of Intensity
350	<i>Pb < Zn < Mn < S < Mg < Na < P < Fe < Si < Ca < K < Al</i>
550	<i>Pb < Zn < Mn < Mg < S < P < Na < Fe < Ca < Si < Al < K</i>
650	<i>Pb < Zn < Mn < Mg < S < Na < P < Si < Fe < Ca < Al < K</i>

4.3.3 Biochar pH, electrical conductivity, exchangeable bases and cation exchange capacity

Biochar pH values in H₂O and KCl and EC are shown in Table 4.6. The values of pH were significantly increased by increase in pyrolysis temperature. Electrical conductivity did not significantly increase from 350°C to 550°C. Calcium, Mg and Na decreased with increase in pyrolysis temperature with Mg being stable from 550°C to 650°C. Potassium was not influenced by any increase in pyrolysis temperature.

Table 4. 6: Exchangeable bases, pH and electrical conductivity of pine-bark biochars

Property	Temperature (°C)		
	350	550	650
pH (H ₂ O)	5.8c	6.8b	7.2a
pH (KCl)	4.5c	7.0b	7.6a
EC (μS cm ⁻¹)	15.2b	15.4b	19.6a
Ca (cmol kg ⁻¹)	2.10a	1.36b	0.66c
Mg (cmol kg ⁻¹)	1.23a	0.21b	0.24b
K (cmol kg ⁻¹)	1.68a	1.61a	1.51a
CEC (cmol kg ⁻¹)	15.00a	5.56b	4.72b

Means followed by the same letter in each row are not significantly different at p<0.05.

4.3.4 FTIR – surface functional groups of the biochar

The carboxylic acid O-H and aldehyde C=O functional group were only present in biochars pyrolysed at 350°C. The ring stretching of aromatic C (C=C-C) and C=C bending of aromatic carbon were persistent throughout the range of pyrolysis temperatures. The phenol O-H tertiary alcohol functional group ($1410\text{-}1310\text{ cm}^{-1}$) only occurred in biochar produced at 550°C. Aromatic P-O-C phosphate functional group ($1240\text{-}1190\text{ cm}^{-1}$) was present in all biochars except the one pyrolysed at 550°C. The other aromatic phosphate functional group ($995\text{-}850\text{ cm}^{-1}$) persisted with increase in pyrolysis temperature. Nitrate and phosphate ions were present in.

4.3.5 Surface area, pore volume and pore size of the biochars

Surface area and pore volume increased with increase in pyrolysis temperature (Table 4.8). The increase of surface area was 83.7% for 350 to 550°C and 7.5% for 550 to 650°C, pyrolysis temperature. On the other hand, the increase in pore volume was 75% for 350 to 550°C, and 3.64% for 550 to 650°C, pyrolysis temperature. Pore size decreased by 34.4% as pyrolysis temperature increased from 350°C to 550°C and by 4.23% from 550°C to 650°C.

Table 4. 7: FTIR spectra of three biochars generated at different pyrolysis temperatures

Wave number cm^{-1}	Actual Functional group	Temperature ($^{\circ}\text{C}$)		
		350	550	650
*3000 – 2500	O-H stretching of carboxylic acid	2822.93		
*1740 – 1690	C=O stretching of aldehyde	1716.66		
*1700 – 1500	C=C bending of aromatic carbon	1562.97	1561.14	1560.67
1510 – 1450	C=C-C ring stretching of aromatic C	1496.85	1496.88	1496.93
1410 – 1310	O-H bending of phenol (tertiary alcohol)		1408.13	
1380 – 1350	Nitrate ions	1356	1355.6	1356.31
1240 – 1190	P-O-C stretching of aromatic phosphates	1220.02		1220.15
1100 – 1000	Phosphate ions	1061.2	1068.09	1069.62
995 – 850	Aromatic phosphates	887.21	955.67	953.77
860 – 680	C-H bending of aromatic C	683.71	772.74	772.63

*Encyclopaedia of Analytical Chemistry (Coates, 2000) & *WebSpectra (Merlic, 1997)*

Table 4. 8: Surface area and pore volume and size of pine-bark biochars

Property	Temperature ($^{\circ}\text{C}$)		
	350	550	650
Surface area ($\text{m}^2 \text{g}^{-1}$)	73.1	449	485
Pore volume ($\text{cm}^3 \text{g}^{-1}$)	0.053	0.212	0.220
Pore size (\AA)	28.8	18.9	18.1

4.3.6 External morphology, porosity and surface area of resultant biochars

Figure 4.1 shows distinctive morphological structure of the biochars. External morphology of the resultant biochars shows good porous structure with some fissures on all biochars (Figure 4.1). These three biochars are dominated by flaky and platy structure with greater abundance at high pyrolysis temperature.

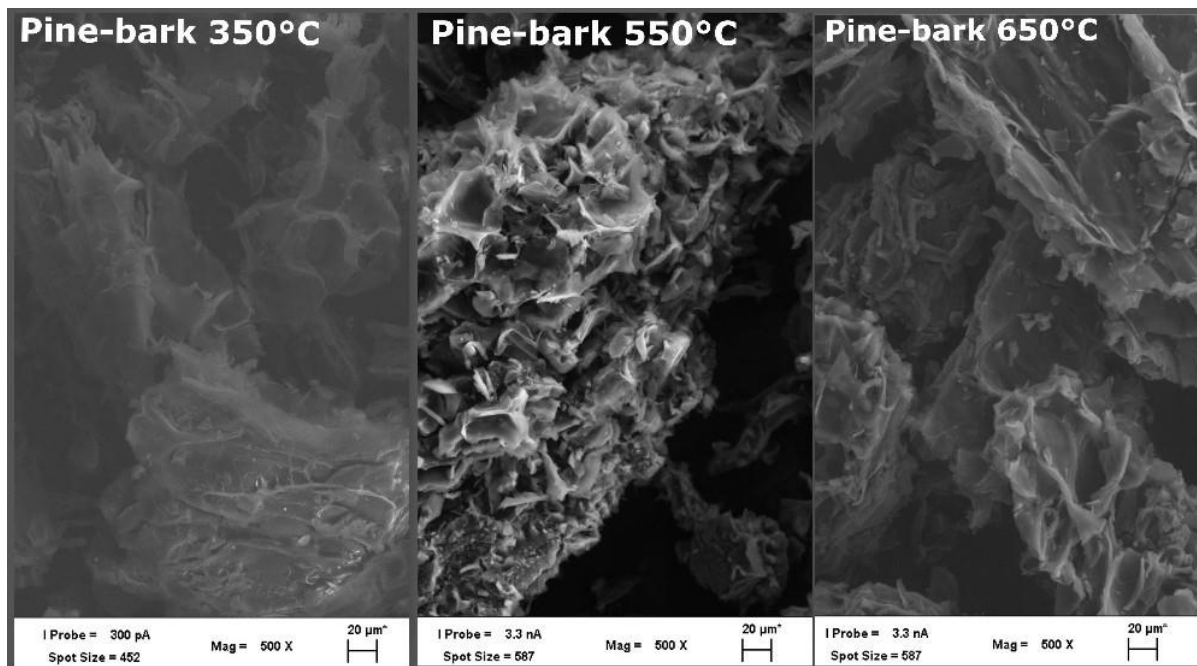


Figure 4. 1: Morphological comparison of six resultant biochar at different pyrolysis temperatures

4.3.7 Cadmium sorption by single biochars

The sorption capacity (S_{max}), the constants relating to bonding energy (b) and the correlation coefficients, (R^2) of different biochars are given in Table 4.9. Sorption of Cd on pine-bark biochars increased with increase in pyrolysis temperature. The coefficients of determination (R^2) are ≥ 0.87 . The constants relating to bonding energy were positive for the biochar at 550°C and negative for the other two pyrolysis temperatures.

Table 4. 9: Cadmium sorption parameter on pine-bark biochar

<i>Pyrolysis temperature (°C)</i>	<i>S_{max} (mg kg⁻¹)</i>	<i>b (L kg⁻¹)</i>	<i>R²</i>
350	20.00	-1.52	0.87
550	29.41	1.79	0.94
650	34.48	-1.71	0.98

4.3.8 Synergetic effect of composite biochars

When pyrolysed at 350°C, the sorption of Cd on biochar was in the order latrine > sewage sludge > pine-bark (Table 4.10). The increase in the proportion of pine-bark biochar in latrine waste: pine-bark biochar combinations resulted in a decrease in the sorption of Cd both at 350 and 650°C. The same trend was observed in sewage sludge: pine-bark biochar combinations. Compared to the expected sorption, based on the proportion and sorption capacity of each biochar in the mixture, the measured sorption was higher in all combinations, except 25% latrine waste and 75% pine-bark biochar pyrolysed at 350°C. For example in the 50% latrine waste and 50% pine-bark biochar at 350°C, the expected sorption was 128 calculated as $(0.5 \times 200) + (0.5 \times 55.6)$. In this case, the measured sorption maximum was 143 mg kg⁻¹ which was higher than the expected value (Table 4.10). This positive effect was higher at 50% latrine waste and 50% pine-bark combination for both 350 and 650°C pyrolysis temperatures, while with sewage sludge biochar the positive effect was highest for the 75% sewage sludge and 25% pine-bark biochar. Constants relating to bonding energy of the biochar combinations decreased with increase pine-bark biochar. The coefficients of determination of the combined biochar types > 0.900.

Table 4. 10: Effects of combinations of biochar from pine-bark and latrine waste or sewage sludge on Cd sorption maxima measured (expected) and *b* value.

Biochar combination	Pyrolysis temperature (°C) combinations	Smax (mg kg⁻¹)	b (L kg⁻¹)	R2
LW: PB				
100% : 0%	350: 350	200 (200)	10	0.861
75% : 25%		167(164)	6	0.950
50% : 50%		143 (128)	1.4	0.953
25% : 75%		83.3 (91.7)	-3	0.973
0% : 100%		55.6 (55.6)	0.06	0.297
LW: PB				
100% : 0%	650: 650	200 (200)	5	0.942
75% : 25%		200 (155)	5	0.928
50% : 50%		167 (110)	6	0.983
25% : 75%		76.9 (64.2)	-2.17	0.975
0% : 100%		18.9 (18.9)	17.67	0.953
SS: PB				
100% : 0%	350: 650	125 (125)	-80	0.995
75% : 25%		125 (96.6)	2.67	0.996
50% : 50%		83.3 (68.1)	1.33	0.982
25% : 75%		41.7 (39.6)	-1.26	0.972
0% : 100%		11.1 (11.1)	-0.54	0.889

4.3.9 Relationship of S_{max} and biochar characteristics

Fixed C, pH and surface area had a strong positive relationship with S_{max}, while total P, total Al and CEC are negatively correlated with Cd sorption (Table 4.11). Over 99% of the variation in Cd sorption on pine-bark biochar was explained by two principal components, with PC1 explaining 89.8% while PC2 explained 10.4%. Fixed C, pH and surface area had significantly positive loadings while total P, total Al and CEC loaded negatively on PC1. Only ash loaded significantly (positive) on PC2.

Table 4. 11: Correlation (CA) and principal component (PCA) analyses of Cd Smax and biochar characteristics

CA								
Variables	1	2	3	4	5	6	7	8
1. Smax (mg kg ⁻¹ Cd)	1.0000							
2. Ash (%)	0.6605	1.0000						
3. Fixed C (%)	0.9989	0.6239	1.0000					
4. pH KCl	0.9747	0.4759	0.9842	1.0000				
5. CEC (cmol kg ⁻¹)	-0.9609	-0.4269	-0.9731	-0.9985	1.0000			
6. Total P (g kg ⁻¹)	-0.9583	-0.4182	-0.9708	-0.9979	1.0000	1.0000		
7. Total Al (g kg ⁻¹)	-0.9380	-0.3592	-0.9535	-0.9917	0.9973	0.9979	1.0000	
8. BET Surface Area (m ² g ⁻¹)	0.9627	0.4326	0.9745	0.9988	-1.0000	-0.9999	-0.9968	1.0000
PCA								
Variables	Comp 1	Comp 2						
1. Smax (mg kg ⁻¹)	0.3500	0.1067						
2. Ash (%)	0.2041	0.8486						
3. Fixed C (%)	0.3513	0.0571						
4. pH KCl	0.3492	-0.1277						
5. CEC (cmol kg ⁻¹)	-0.3463	0.1843						
6. Total P (g kg ⁻¹)	-0.3457	0.1941						
7. Total Al (g kg ⁻¹)	-0.3408	0.2592						
8. BET Surface Area (m ² g ⁻¹)	0.3467	-0.1778						
<i>Eigenvalue</i>	8.0787	0.9213						
<i>Proportion</i>	0.8976	0.1042						

4.4. Discussion

The decrease in biochar yield with pyrolysis temperature could be attributed to the loss of organic C associated with thermal degradation of lignocellulosic biomass and dehydration of organic compounds (Liu et al., 2014). Decline in pine-bark biochar yield is associated with dehydration of organic compounds such as the hydroxyl groups – phenols and carboxylic acid; other studies report (Liu et al., 2014; Ahmad et al., 2012; Novak et al., 2009; Parihar et al., 2007). At lower pyrolysis temperature, biochar yields were higher due to minimal losses of C, H₂ and CH₄ (Liu et al., 2014; Mitchell et al., 2013; Novak et al., 2009). The decrease was in agreement with findings of other studies on orchard pruning biomass (Baronti et al., 2014) spruce chips (Mitchell et al., 2013) pine wood (Enders et al., 2012) hardwoods (Brewer et al., 2011) and eucalyptus wood (Singh et al., 2010). Low ash content (2.5 to 3.1%) and high volatiles, indicated that the material was rich in decomposable carbon.

The increase in biochar pH with pyrolysis temperature could be explained by the degradation of organic acids, formation of recalcitrant molecules and the production of ash (Enders et al., 2012; Buamscha et al., 2007). Increase in pyrolysis temperature has been shown to result in production of alkaline biochars (Liu et al., 2014). The pH values obtained from pine-bark biochar were in agreement with those reported by Tucker (1995) and Enders et al (2012), who reported that pine wood biochar pH was below 7.5 at 600°C. Furthermore, increased from pH 4 to 7 with increase in pyrolysis temperature, without significant increase in ash content, was also consistent with Tucker (1995) and Enders et al. (2012). The high biochar pH at higher pyrolysis temperature suggest that the biochar has potential liming effects when added to acidic soils and could facilitate precipitation of heavy metals in industrial effluents. The decrease in H led to a decrease in hydrogen/carbon molar ratio, an index of biochar aromaticity. Hmid et al. (2014) and van Zwieten et al. (2010) reported that biochars become more aromatic and carbonatious at high temperature due to a decline in H/C (Kloss et al., 2012). Biochar pyrolysed at 350°C appears to fix lower C and is unlikely to sequester a lot of C when added to soil system comparative to

higher pyrolysis temperature counterparts. The increase in C/N ratio with increase in pyrolysis temperature indicated that the biochar became more recalcitrant. As pyrolysis temperature increases, already existing high C in the form of lignin, cellulose and hemicellulose, is converted into more stable, aromatic and recalcitrant form while on the other hand, low and volatile N is being lost attributed to thermal degradation of biomass (Cantrell et al., 2012) hence increasing C:N ratio. Increase in surface areas and porosity with increase in pyrolysis temperature could be explained by escape of volatile compounds from the feedstock. Increasing pyrolysis temperature enhances the intensity and strength of volatilization of volatile components, leading to improvement in the porosity of the carbonized biomass (Ahmad et al., 2012; Downie et al., 2011). Kim et al. (2013) found that increase in pyrolysis temperature, greatly increased pH and surface area. An increase in surface area and micro-porosity due to pyrolysis, suggests that water holding capacity, nutrient retention and as well as microbial biodiversity and functions could be enhanced (Masto et al., 2013).

The higher fixed C and increase in C/N of pine-bark biochar with pyrolysis temperature indicated that pine-bark biochar is more important for C sequestration as it is more recalcitrant. This could be essential for C sequestration of high activity C (high surface area and CEC) from pine-bark. The significance of pH and CEC patterns may be explained by loss of acid functional group; O-H stretching of carboxylic acid (Enders et al., 2012). The O-H stretching of carboxylic acid at 350°C may have been converted to O-H bending of phenol (tertiary alcohol) as pyrolysis temperature increased to 550°C. Furthermore, P-O-C stretching of aromatic phosphate ($1240 - 1190\text{ cm}^{-1}$) that got diminished at 550°C may be linked with a slight increase in the intensity of aromatic phosphates ($995 - 850\text{ cm}^{-1}$) at 550°C.

Biochar performance as sorbents depends on the chemical composition and surface characteristics, which in turn are influenced by biochar preparation and feedstock (Li et al., 2014). The positive correlation between Cd sorption and biochar ash content pH, surface area and fixed C suggested that these parameters are essential for increasing sorption of this metal. The positive correlation of Cd sorption with ash content could be a result of exchange reactions with carbonates and other minerals

in the ash (Inyang et al., 2016). This was in agreement with Xu and Chen (2014) who suggested that minerals in the ash dominated the sorption process. Mohan et al (2007) reported that an increase in pH led to an increase in adsorption of metals wood biochar. The change in biochar pH could have influenced the surface functional groups of the biochar. From the results on Table 4.7, the O-H group of carboxylic acid and the C=O of aldehyde were lost by increasing pyrolysis temperature to 550 and 650°C. Li et al. (2017) reported that for biochar with low CEC, complexation with oxygenated functional groups is an important sorption mechanism for Cd. The contribution of the surface functional groups could have been enhanced by increase in surface area. A review of literature by Li et al. (2017) concluded that surface area was among the most important factors affecting metal sorption on biochar. This view is in agreement with findings from this study which showed that Cd sorption and surface area of pine-bark biochar increased with pyrolysis temperature.

Angelo et al (2014) indicated that changing the biochar's surface chemistry through oxidation may increase retention of metal ions. In some other studies, it is reported that removal of Cd was least influenced by biochar morphology and specific surface area (Trakal et al., 2014). Based on the results of this investigation, these findings are almost in agreement with those Trakal et al. (2014). Furthermore, several other studies reported that pyrolysis temperature influences sorption capacities of different biochars (Trakal et al., 2014; Xu et al., 2013; Inyang et al., 2012; Kolodynska et al., 2012). The results of this study were contrary to other studies, which reported that increase in CEC significantly enhanced Cd removal efficiency of various biochar types (Forjan et al., 2016; Puga et al., 2016; Qian et al., 2016; Bogusz et al., 2015; Trakal et al., 2014). The difference could be explained by differences in the characteristics of feedstocks used (pine-bark in this study), which affected the properties of biochar.

The higher Cd sorption in the combinations of pine-bark and latrine waste or sewage sludge biochar, compared to expected levels based on proportions and sorption capacities, indicated synergistic behaviour of the component biochars. In Chapter 3, ash and total P content of latrine waste and sewage sludge biochar types were

positively correlated with Cd sorption, while increase in pH negatively affected sorption. In this chapter (Chapter 4) ash content, pH and surface area are positively correlated with Cd sorption pine-bark biochar. The positive effects of pH and surface area on Cd sorption on pine-bark biochar, while increase in pH decreased sorption on latrine waste and sewage sludge biochars (no effects of surface area), indicates that the mechanisms of sorption are different. Combining the latrine waste (or sewage sludge) biochar, having higher ash and phosphorus, with pine-bark biochar, with higher surface area, could have benefited from both precipitation of phosphates of carbonates and phosphates of Cd and interactions with surface functional groups (Li et al. 2017). The combination could also have modified the surface functional groups and enhanced sorption. The highest synergistic effect at 50% latrine waste and at 75% sewage sludge biochar indicates that these biochar types need to be mixed with pine-bark biochar at these rates for the best removal of Cd from solution.

4.5. Conclusions

Biochar yield, volatile matter and CEC were decreased, while fixed C, surface area and porosity were increased by increase in pyrolysis temperature. Increase in pyrolysis temperature resulted in increase in Cd sorption in pine-bark biochars. In mixtures, pine-bark biochar had synergistic effects with latrine waste or sewage sludge biochar, particularly at 50% latrine waste biochar or 75% sewage sludge biochar. Complementary research on sorption of other heavy metals on faecal waste and pine-bark biochar, in laboratory-made single metal solutions and multiple metal effluents, is recommended.

CHAPTER 5: SORPTION OF SELECTED HEAVY METALS WITH DIFFERENT RELATIVE CONCENTRATIONS IN INDUSTRIAL EFFLUENT ON BIOCHAR FROM HUMAN FAECAL PRODUCTS AND PINE-BARK

5.1 Introduction

Environmental contamination with heavy metals poses risks to the biosphere (Prasad, 1995; Pelleria and Gidarakos, 2015) and mankind health (Ghosh and Singh, 2005; Liang et al., 2011), with the soil-plant-human pathway being a primary mechanism of transfer. Anthropogenic activities such as mining, agriculture and other industrial activities result in elevated levels of heavy metals in soils (Prasad, 1995; Kabata-Pendias, 2000; Coumar et al., 2016). For example, industries specializing in electroplating and production of batteries, fertilizers and pesticides produce wastewater, which often contains high concentrations of heavy metals (Prasad, 1995; Perez-Marin et al., 2007; Mohan et al., 2007). The discharge of the effluents into sewer systems enriches sewage sludge with the metals, which presents challenges for land disposal of the sludge. The occurrence of multiple heavy metals, from different sources, and their non-biodegradability and persistence in the environment, exacerbate the disposal challenges and poses major ecological risks (Cui et al., 2015). Treatment of industrial wastewater, at source, makes it safer for discharge into the environment and reduces environmental pollution (Ranade and Bhandiri, 2014, Gonzalez et al., 2016).

Precipitation and complexation are known to be the most effective strategies in removal of metals from effluents but the requirement of specialized reagents and expensive equipment makes them too expensive (Perez-Marin et al., 2007; Shi and Cai, 2009; Mohan et al., 2014). Other available technologies for treatment of wastewater, including membrane filtration, ozonation, advanced oxidation and adsorption, have also shown high effectiveness (Doble and Kumar, 2005; Ranade and Bhandiri, 2014; Gonzalez et al., 2016), but the high costs also limit their

application. Biochar has shown potential to be a cost-effective biosorbent for the removal of toxic metals from aqueous solutions and wastewater (Namgay et al., 2010; Major, 2011; Kim et al., 2013; Mohan et al., 2014; Coumar et al., 2016). The effectiveness depends on biochar characteristics owing to properties of the feedstock and pyrolysis conditions (Li et al., 2014; Trakal et al., 2014; Bogusz et al., 2015; Kuppusamy et al., 2016).

Studies by McKay and Porter (1997), Chen et al. (2011) and Xu et al. (2013) have shown the capacity of different biochar types to remove heavy metals such as Cd, Cu and Zn from aqueous solution. Biochar types from nut shells, plum stones, wheat straws and grape stalks and husks were highly effective in removal of Cd from aqueous solution, with wheat straw and grape husk and stalks being the most efficient (Trakal et al., 2014). Biochar produced at higher pyrolysis temperature has been shown to increase Cd sorption capacity of biochar due to higher aromatic structure, pH and surface area (Kim et al., 2012; Kim et al., 2013). It is essential to note that most of the studies on the removal of metals by biochar were done with single metals (Chen et al., 2011; Xu et al., 2013) with fewer on mixtures of metals, at equal concentrations, in aqueous solutions. There is evidence that presence of competing metals in aqueous solution affect the sorption of individual metals. For example, the adsorption capacities of metals from aqueous solution onto sesame straw biochar were in the order of $Pb > Cd > Cr > Cu > Zn$ from single-metal and $Pb > Cu > Cr > Zn > Cd$ multi-metal solutions (Park et al., 2016). Where multiple metals were used, the mixtures are often prepared with equal concentrations (Park et al., 2016). However, in reality, the metals occur at different concentrations in industrial effluents, and the concentration effects may affect the preferential uptake of metals by sorbents.

In a study on sorption and desorption of heavy metal on biochar and commercial activated carbon, Kolodynska et al. (2017) reported that various operating factors such as adsorbent dose and initial concentration are influential on the sorption. In that study, sorption capacity increased with increase in initial concentration of metal ions (Kolodynska et al., 2017). There is need to understand the potential of using different

types of biochar from locally available feedstocks on removal of multiple metals from a typical industrial effluent.

In preliminary studies, biochar from human faecal wastes (Koetlisi and Muchaonyerwa, 2017; Chapter 3) differed in their physicochemical properties, with higher cadmium (Cd) sorption capacity, compared to those from pine-bark (Koetlisi and Muchaonyerwa, 2018; Chapter 4). The Cd sorption generally declined with increase in pyrolysis temperature (350 to 650°C) from 200 to 167 for latrine waste biochar, and from 143 to 36 mg kg⁻¹ for sewage sludge biochar, while it slightly increased from 20 to 34 mg kg⁻¹ for pine-bark biochar. Whereas ash content and phosphorus composition explained the sorption of Cd on faecal biochar, fixed C, pH and BET surface area appeared to be more important in pine-bark biochars. The potential of these biochar types to remove mixtures of heavy metals from industrial effluents needs to be understood. Therefore, the objective of this study was to determine effects of biochar types from human faecal waste and pine-bark on sorption of multiple metals from industrial effluent and single metal aqueous solutions.

5.2. Materials and Methods

5.2.1 Biochar

The biochar types used in this study were produced from two faecal wastes (sewage sludge and latrine waste) and pine-bark. The details of the biochar types, production conditions and characteristics, are given in Chapter 3 (faecal waste) and Chapter 4 (pine-bark). Selected characteristics of the biochars are shown in Table 5.1.

5.2.2 Industrial effluent

Untreated industrial effluent was obtained from ES & LC Manufacturing, an electroplating company in Pietermaritzburg (29°39'03.03"S and 30°24'43.53"E). The company specializes in satellite mounting brackets and electroplating. The effluent was analysed for pH, electric conductivity (EC), total dissolved solids (TDS), and

chemical oxygen demand (COD), according to standard methods (American Public Health Association, 1995). Total elemental composition of the effluent was analysed using the inductively coupled plasma-mass spectrometer (ICP-MS) (Ra et al., 2016). This effluent had low pH, high electrical conductivity and a variety of heavy metals, as indicated in Table 2. Three metals had concentrations higher than the critical limits for disposal into the environment and were in the order Zn > Cu > Cr.

Table 5. 1: Selected physicochemical properties of biochars used in this study

Biochar	pH (KC)	Ash (%)	Fixed C (%)	Volatile (%)	Total P (g kg ⁻¹)	BET (m ² g ⁻¹)
<i>Latrine waste</i>						
350	6.9	84.3	5.5	10.27	25.3	7.54
550	7.1	89.9	4.4	5.70	24.9	23.7
650	7.3	92.7	4.2	3.10	25.0	25.7
<i>Sewage sludge</i>						
350	6.0	49.2	14.6	31.13	22.6	0.29
550	7.7	66.2	23.9	9.80	38.1	1.58
650	8.0	69.4	23.3	7.23	37.9	4.21
<i>Pine-bark</i>						
350	4.3	2.6	57.6	39.47	0.45	73.1
550 *	7.4	2.5	77.3	20.27	0.32	449
650 *	7.9	3.1	86.1	10.80	0.31	485

**Biochars from pine-bark produced at 550 and 650°C were not used in this study.*

Table 5. 2: Electrical conductivity, pH and concentrations of heavy metals in the effluent used

Parameters	Critical limit (DWAF, 2004 In Rodda et al., 2010)	Effluent
pH	5.5 - 9.5	2.5±0.0
EC (mS m ⁻¹)	70 - 150	1383±4.2
COD (mg O ₂ L ⁻¹)	< 75	510±36.8
Cr (µg L ⁻¹)	<0.05	1.25±0.02
Cu (mg L ⁻¹)	<0.01	10.2±0.24
Zn (mg L ⁻¹)	<0.10	212±13.8

Critical limits (DWAF, 2004). Metal ratios: Zn: Cu =21:1, Zn: Cr =170:1, Cu: Cr = 8:1.

5.2.3 Sorption of elements from effluent with multiple metals by biochars

The batch sorption study with biochar from latrine waste, sewage sludge and pine-bark biochar, pyrolysed at 350°C, with Zn solutions (0, 5, 10, 15, 20, and 25 mg L⁻¹ in 0.01 M CaCl₂) was done as detailed in Section 3.2.6. The same batch sorption study was repeated with solutions of Cu and Cr, at the same concentrations as Zn.

Another batch sorption study with latrine waste and sewage sludge biochar pyrolysed at 350 550 and 650°C with dilutions of industrial effluent, also as described in Section 3.2.6. Biochar (2.5 g) was mixed with 25 mL of 0, 6.25, 12.5 and 25% for Zn and 0, 12.5, 25, 50, 75 and 100% of the effluent for Cu and Cr. The effluent was diluted to the selected metal concentrations with 0.01 M CaCl₂ solution (background electrolyte). These dilutions corresponded to 0, 13.3, 26.5 and 53.0 mg L⁻¹ for Zn; 0, 0.638, 1.28, 2.55, 5.10, 7.65 and 10.2 mg L⁻¹ for Cu; and 0, 0.078, 0.156, 0.313, 0.625, 0.938 and 1.25 mg Cr L⁻¹. The batch sorption study with the effluent was repeated with biochar produced from the same feedstocks pyrolysed at 550 and

650°C. The concentrations used for Cu were 0, 1.28, 2.55, 5.10, 7.65 and 10.2 mg L⁻¹, while for Cr, the 0, 0.313, 0.625, 0.938 and 1.25 mg L⁻¹ concentrations were used. To estimate the sorption capacity and parameter related to energy of bonding of heavy metals onto biochar, the experiment, data were fitted to the Langmuir sorption model (Kumar et al., 2011; Xu et al., 2013). Sorption data that did not fit in Langmuir were fitted in Freundlich model (Appendix 2).

The solid retained on the filter paper was collected for Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS) to determine abundance of specific available and adsorbed elements (Xu et al., 2013). The sorption study was repeated with single metal solutions (Cu, Zn and Cr at 0, 5, 10, 15, 20 and 25 ppm concentrations) prepared in 0.01 M CaCl₂ and the three biochars pyrolysed at 350°C to determine whether the presence of other metals in the effluent had affected sorption on the biochars. The multi-metal sorption studies were repeated using biochars produced at 550 and 650°C from latrine waste and sewage sludge, and pine-bark biochars were not used because they showed low Cd (Chapter 4), and when pyrolysed at 350°C, Zn and Cu sorbed was low.

5.2.4 Surface characteristics of resultant biochars

The ZEISS EVO LS15 scanning electron microscopy-energy dispersive x-ray spectroscopy (SEM) was used to analyse the external morphology and qualitative chemical composition of biochars. This was done as detailed in Section 4.2.3.

5.2.5 Statistical analysis

Stepwise regression derived from multiple regression analysis was used to determine the combined effect of biochar parameters on metal sorption capacity from the industrial effluent. The analysis identified the best-fit model by removing certain variables based on the t-statistics for estimated coefficients (Gray et al., 1999).

5.3. Results

5.3.1 Sorption of Zn from multiple metal effluent and single metal solutions

Based on the shape of the sorption isotherms, biochar from pine-bark had lower affinity for Zn than those from latrine waste and sewage sludge pyrolysed at 350°C, both when the multi-metal effluent (Figure 5.1a) and single metal solution (Figure 5.1b) were used. Sorption maxima of Zn was higher on latrine waste and sewage sludge than pine-bark biochar, both for multiple metal effluent and single metal solution (Figure 5.2a and b). Pine-bark biochar was about 100 times less effective on Zn sorption compared to faecal biochar. However, latrine waste biochar sorbed more Zn from single metal solution than from multi-metal effluent, than biochar from sewage sludge. The sorption maximum values for faecal biochar types were lower for single metal solutions than multiple metal effluent, while for pine-bark biochar, the sorption maximum was higher for single metal solution. Biochar from latrine waste and sewage sludge pyrolysed at 550 and 650°C exhibited lower affinity for Zn from multi-metal effluent than the same feedstocks pyrolysed at 350°C. Pyrolysis at 650°C resulted in lower Zn affinity for latrine waste biochar and higher affinity for sewage sludge biochar than biochar pyrolysed at 550°C (Figure 5.1c; Appendix 2). The maximum sorption of Zn on latrine waste biochar declined from 312.5 to 192.3 mg kg⁻¹ with increasing pyrolysis temperature from 350 to 550°C, with no further change at 650°C (Figure 5.2b). Increasing pyrolysis temperature did affect Zn sorption on sewage sludge biochar. The constant related to bonding energy was higher on pine-bark than faecal biochar and was also higher for single metal solutions than the effluent (except latrine waste) (Table 5.3). While maximum sorption values were similar between latrine waste and sewage sludge biochar, the bonding energy was higher for sewage sludge biochar. Coefficients of variation for faecal biochar types (350°C) were > 0.90 and was 0.56 for pine-bark biochar from multiple metal effluent. However, constants related to bonding energy declined with increase in pyrolysis temperature for both latrine waste and sewage sludge biochar. Coefficients of variation were lower than 0.90 for at the 550°C pyrolysis temperature, for both latrine waste and sewage sludge biochar.

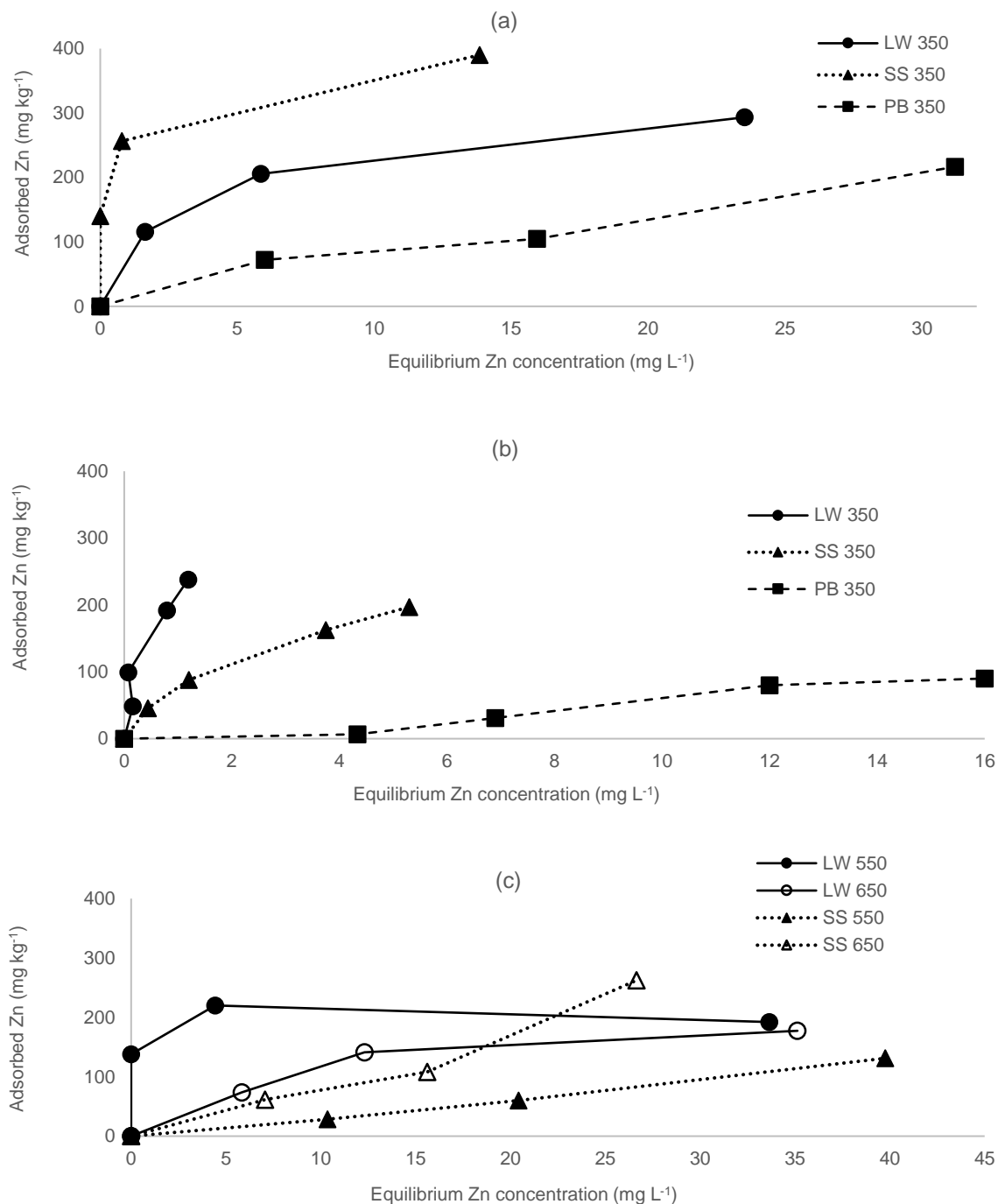


Figure 5. 1: Sorption isotherms of zinc (a) from effluent on biochar pyrolysed at 350°C, (b) single metal on biochar pyrolysed at 350°C and (c) from effluent on biochar pyrolysed at 550 and 650°C; also shown in Appendix 2.

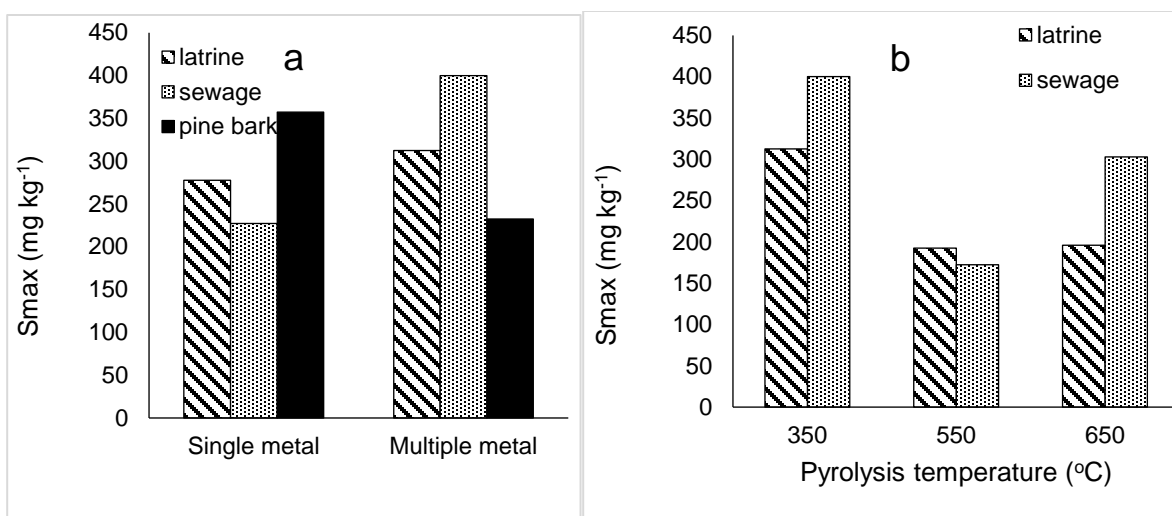


Figure 5. 2: Maximum zinc sorption on faecal and pine-bark biochar pyrolysed at 350°C (a) and on faecal biochar at increasing pyrolysis temperatures (b).

Table 5. 3: The b (L kg⁻¹) and r^2 values of linearized Langmuir models of zinc on biochars from latrine waste, and sewage sludge pyrolysed at 350°C (a) and on faecal biochar at increasing pyrolysis temperatures (b).

Biochar feedstock	b-value and (r ²)	
	Source of metals (350° C pyrolysis)	
	Aqueous solution	Effluent
Latrine waste	3.6 (0.77)	0.55 (0.98)
Sewage sludge	0.86 (0.90)	5.00 (1.00)
Pine-bark	0.01 (0.01)	0.11 (0.68)
	Pyrolysis temperature (metals from effluent)	
	550°C	650°C
Latrine waste	-3.71 (1.00)	0.22 (0.94)
Sewage sludge	0.04 (0.34)	0.07 (0.38)

5.3.2 Sorption of Cu from multiple metal effluent and single metal solutions

Similarly to Zn, the shape of the sorption isotherms shows that pine-bark biochar had lower affinity for Cu than those from latrine waste and sewage sludge pyrolysed at 350°C, both for the effluent (Figure 5.3a) and single metal solution (Figure 5.3b). Affinity for Cu from single metal solution was higher for latrine waste biochar than sewage sludge biochar, while for the effluent sewage sludge biochar had greater affinity. The sorption maxima of Cu from single metal solution was higher for latrine waste biochar and lower for pine-bark biochar when compared with those of multi-metal effluent, with no differences for sewage sludge biochar (Figure 5.4). Also similar to Zn, maximum sorption of Cu was higher for biochar from latrine waste and sewage sludge than pine-bark biochar, both for the effluent and single metal solution. Copper sorption was higher for single metal solution than multiple metal effluent. Sorption of Cu from multi-metal effluent was lower on latrine waste biochar than sewage sludge, while for single metal solution, sorption on latrine waste biochar was higher (149.6 mg kg⁻¹) then on sewage sludge (128.4 mg kg⁻¹). Also similar to Zn, the constant related to bonding energy was higher for single metal solutions than the effluent, except pine-bark biochar (Table 5.4). Latrine waste biochar had the highest bonding energy constant while pine-bark biochar had the lowest. All coefficients of variation were >0.95, except for Cu sorption on latrine waste biochar from single metal solution.

Maximum sorption of Cu from effluent decreased with increasing pyrolysis temperature for the faecal biochar types, with 200 mg kg⁻¹ at 350°C and 23 mg kg⁻¹ at 650°C sewage sludge biochar. On latrine waste biochar, Cu sorption was only decreased by increasing pyrolysis temperature from 550 to 650°C. The highest b-values were for biochar produced at 550°C for both latrine waste (10 L kg⁻¹) and sewage sludge (1.88 L kg⁻¹) biochar and were lower at 650°C pyrolysis temperature (Table 5.4). The least b-values were for biochar produced at 350°C for both feedstocks. The only coefficients of variation that were <0.9 were those on biochar produced at 650°C. Pine-bark 550°C and 650°C were not tested for metal sorption following their low metal sorption affinities at 350°C.

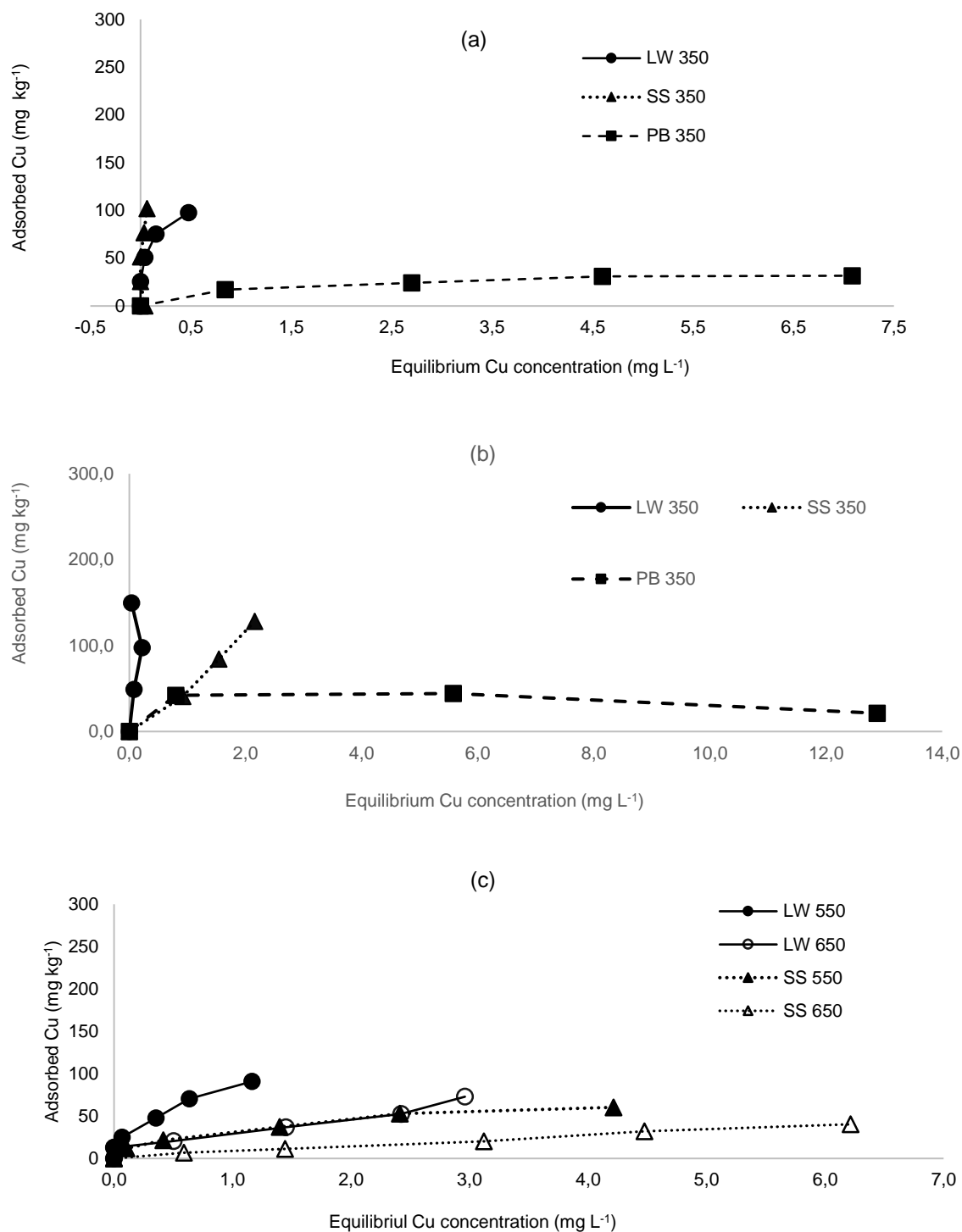


Figure 5. 3: Sorption isotherms of copper from (a) effluent on biochar pyrolysed at 350°C, (b) single metal on biochar pyrolysed at 350°C; also shown in Appendix 2 and (c) effluent on biochar pyrolysed at 550 and 650°C.

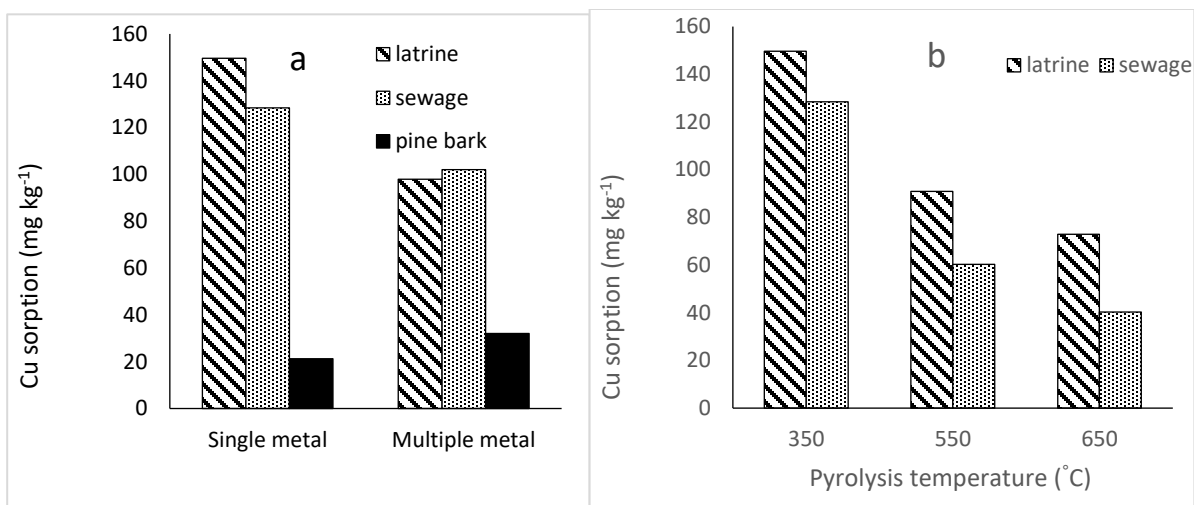


Figure 5. 4: Maximum copper sorption on faecal and pine-bark biochar pyrolysed at 350°C (a) and on faecal biochar at increasing pyrolysis temperatures (b).

Table 5. 4: The b (L kg⁻¹) and r^2 values of linearized Langmuir models of copper on biochars from latrine waste, and sewage sludge pyrolysed at 350°C (a) and on faecal biochar at increasing pyrolysis temperatures (b).

Biochar	b-value and (r ²)	
Source of metals (350° C pyrolysis)		
	Aqueous solution	Effluent
Latrine waste	51.5 (0.84)	32.7 (0.99)
Sewage sludge	1.22 (0.46)	510 (0.97)
Pine-bark	-1.25 (0.95)	1.97 (0.98)
Pyrolysis temperature (metals from effluent)		
	550°C	650°C
Latrine waste	5.67 (0.92)	1.15 (0.75)
Sewage sludge	1.82 (0.95)	0.32 (0.58)

5.3.3 Sorption of Cr from multiple metal effluent and single metal solutions by biochar

The adsorption isotherms for Cr on latrine waste, sewage sludge and pine-bark biochar types are shown in Figure 5.5. The isotherms fitted well in Langmuir model. The maximum sorption of Cr was higher (at least 8 times) for single metal solutions than multiple metal effluent for all biochars (Figure 5.6). Sorption maxima of Cr from single metal solution were in the order latrine waste > pine-bark > sewage sludge, while that from multiple metal effluent was in the order sewage sludge > latrine waste > pine-bark. The constant related to bonding energy was lower for single metal solutions than the effluent for all biochar types pyrolysed at 350°C. The coefficient of bonding energy was highest for pine-bark followed by latrine waste. The isotherm suggests that all the Cr was removed (sorbed), leaving no Cr in solution, as such a sorption maximum could not be calculated because of lack of fit to the Langmuir isotherm (Figure 5.6c). On sewage sludge, Cr sorption declined with increase in pyrolysis temperature, with the highest bonding energy coefficient (79 L kg⁻¹) for the 350°C biochar, and lower (1.0 L kg⁻¹) for higher temperatures. Again, Cr sorption by latrine waste at 350°C from the effluent did not fit Langmuir model (Table 5.5).

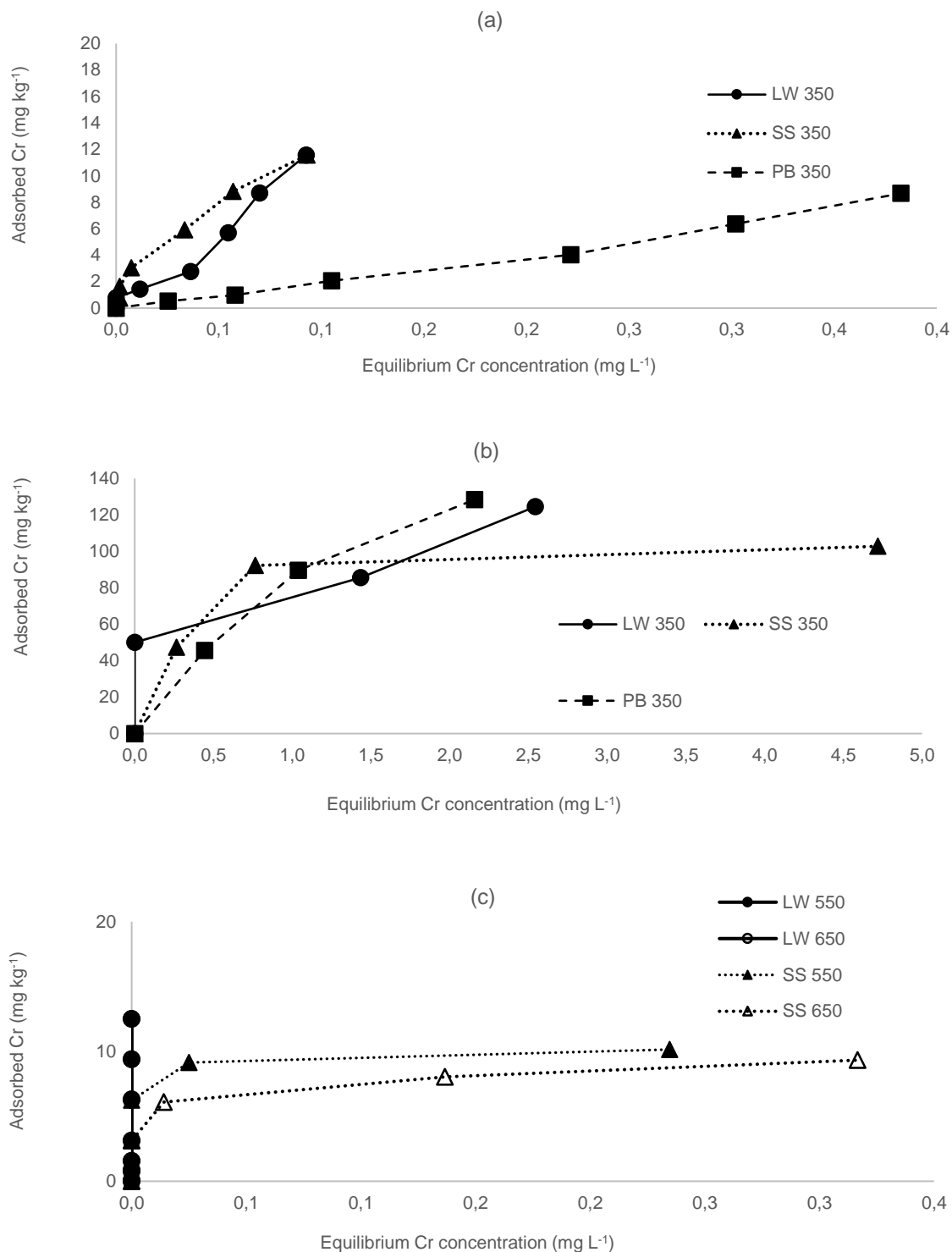


Figure 5. 5: Sorption isotherms of chromium from (a) effluent on biochar pyrolysed at 350°C, (b) single metal on biochar pyrolysed at 350°C; also shown in Appendix 2 and (c) effluent on biochar pyrolysed at 550 and 650°C.

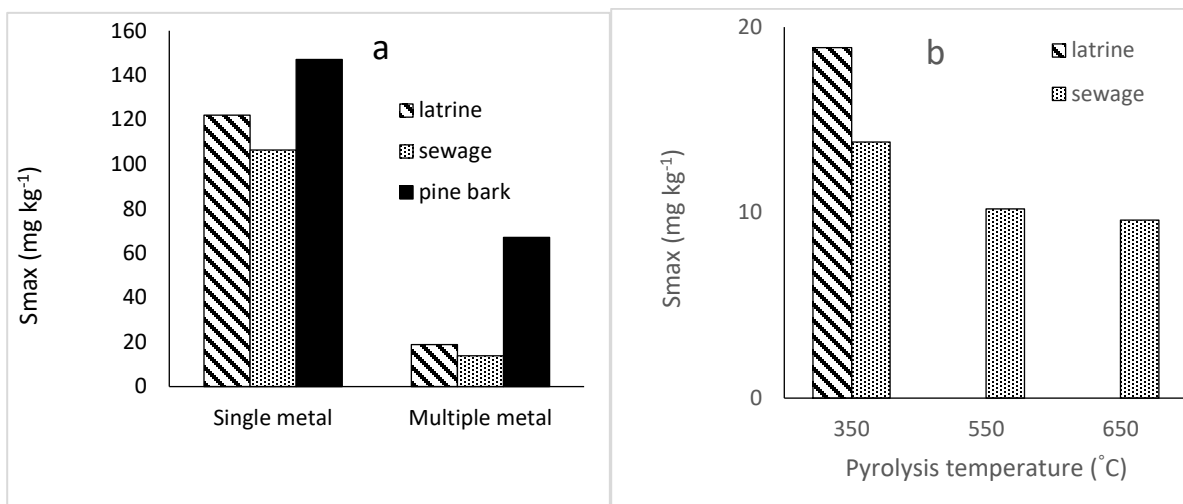


Figure 5. 6: Maximum chromium sorption on faecal and pine-bark biochar pyrolysed at 350°C (a) and on faecal biochar at increasing pyrolysis temperatures (b).

Table 5. 5: The b (L kg^{-1}) and r^2 values of linearized Langmuir models of chromium on biochar from latrine waste, and sewage sludge pyrolysed at 350°C (a) and on faecal biochar at increasing pyrolysis temperatures (b).

Biochar feedstock	b-value and (r^2)	
	<i>Source of metals (350°C pyrolysis)</i>	
	Aqueous solution	Effluent
Latrine waste	5.47 (0.92)	9.64 (0.19)
Sewage sludge	6.71 (1.00)	38.26 (0.92)
Pine-bark	2.06 (0.83)	0.29 (0.31)
	<i>Pyrolysis temperature (metals from effluent)</i>	
	550°C	650°C
Latrine waste*	-	-
Sewage sludge	980 (1.00)	64.81 (1.00)

*No Cr sorption occurred on latrine waste biochar at 550 and 650°C.

5.3.4 SEM-EDS chemical composition of biochars with sorbed metals

Major elements from the EDS spectra are tabulated in Table 5.6 with C and O being dominant for all biochar types. Molar O:C ratios of the biochars were highest on latrine waste and least on pine-bark biochar. Where sorption was done with effluent (50% dilution), the concentrations of Zn, Cu, and Cr were higher than in the control for latrine waste and sewage sludge biochar, with only Cr detected on pine-bark biochar.

Table 5. 6: Concentrations of carbon, oxygen, copper, chromium and zinc (%) on biochar types pyrolysed at 350°C after sorption study with or without effluent

Solution used for sorption	Element (weight %)	Biochars		
		Pine-bark	Sewage sludge	Latrine waste
No effluent	C	71.9	60.9	33.95
	O	28.1	29.0	42.74
	O:C	0.29	0.36	0.94
	Cu	*	0.01	*
	Cr	*	0.06	*
	Zn	*	0.05	*
50% effluent	C	74.6	61.7	43.9
	O	25.4	28.8	40.8
	O:C	0.26	0.35	0.70
	Cu	*	0.07	0.09
	Cr	0.03	0.08	0.18
	Zn	*	0.21	0.09

* indicate non-detection of the metals

5.4 Discussion

The higher Zn and Cu sorption maxima of biochar from latrine waste and sewage sludge than pine-bark biochar, both for multiple metal effluent and single metal solution, could be related to biochar characteristics as affected by feedstock. Faecal biochar had higher ash, P content and pH than pine-bark biochar, which could have supported precipitation. Zhou et al. (2016) reported that peanut-shell biochar with ash had higher Cu sorption than where the ash was removed. The relationship of Zn

sorption with ash content of biochar was also in agreement with Qian et al. (2016), who reported that higher ash released hydroxide and carbonates, which formed precipitates with Zn. Hegazi (2013) also reported that effective removal of metals, including, Cu was increased by higher ash content, with precipitation of the metals on biochar occurring due to phosphates, carbonates and hydroxides (Xu et al., 2013; Zhou et al., 2016). The higher ash, P and pH in the latrine waste and sewage sludge biochar types used in this study, could, therefore, have facilitated precipitation of Zn and Cu (pH 2 – 4 (Sampaio et al., 2009)). Although sewage sludge biochar had lower ash than that from latrine waste, the higher P could have contributed in greater precipitation. The trend of Cu sorption on the biochar types was in agreement with Trakal et al. (2014), who reported that dairy manure biochar was more efficient in removing Cu than that from plant (rice husk) material. The sorbed Cu and Zn were supported by results of SEM-EDS, where the elements were higher than in the control. The ash content of pine-bark biochar was too low to cause significant precipitation of Zn and Cu sorption. Based on these results, biochar from sewage sludge would be more effective as a sorbent to remove Zn and/or Cu from multi-metal effluents where any of these metals are dominant, while latrine waste biochar would be more effective for single metal solutions.

The higher Cr sorption capacity of biochar from pine-bark than from sewage sludge, in single metal solutions, suggests that a different mechanism from those of Zn and Cu, on this biochar. This trend was similar to that of surface area. Ding et al. (2014) reported that hydroxyl and methyl functional groups were essential for the sorption and reduction of Cr(VI) to Cr(III), which precipitates with phosphate. Complexation, an important mechanism for Cr sorption (Li et al., 2017), depends on the abundance of these functional groups, which in this research, declined with pyrolysis temperature on pine-bark biochar as shown in Table 4.7. The isotherms suggests that all the Cr was retained on latrine waste biochar at higher pyrolysis temperatures and this suggest that these important chemical functional groups (hydroxyl and methyl) were effective (Ahmed et al., 2017; Zhou et al., 2017), as indicated by the decline in atomic ratio of H/C. The results of Cr sorption suggested that, in effluents where Cr is the

dominant pollutant, pine-bark biochar would be more appropriate as a sorbent than biochar from latrine waste and sewage sludge.

The higher Zn sorption on biochar produced at 350°C in multi-metal than single metal system was contrary to most literature (Park et al., 2016). Although Park et al. (2016) reported higher sorption of Cu than Zn in binary solution with equal concentrations of the two metals, competition with Zn at 20 times higher concentration, could have suppressed Cu sorption. Metal concentration play a significant role in the rate of adsorption (Mishra et al., 2017). The higher Zn and lower Cu and Cr sorption, in the multi-metal than single metal solutions, indicated that competitive sorption of the metals was affected by relative concentrations in the effluent, which favoured Zn sorption. The extremely higher Zn in the effluent than Cu and Cr could have precipitated with the hydroxides, carbonates and phosphates from the ash at the expense of Cu and Cr, which remained in solution. Competitive sorption of metals by different biochars has been reported previously (Park et al., 2016). Park et al. (2017) indicated that single-metal system of Zn resulted in 38.6 mg g⁻¹ sorption while binary-metal system, with equal concentrations with Cu, yielded 7.9 mg Zn g⁻¹ on rice straw biochar. Zhou et al. (2017) also reported that Zn sorption on sewage sludge biochar was 5.91 and 2.48 mg g⁻¹ in mono-metal and multi-metal solution, respectively.

In the current study, the lower Zn sorption values in single metal solution than in multiple metal effluent, except for pine-bark, could be attributable to high Zn concentration, which was higher than the other elements. Mishra et al. (2017) reported that adsorbent dosage and metal concentration play a significant role in the rate and quantity of adsorption (Mishra et al., 2017). Park et al. (2017) also reported lower values of Cu sorption in multi-metal (40.2 mg g⁻¹) than single metal solutions (56.5 mg g⁻¹) due to competitive sorption with co-existing metals (Li et al., 2017) especially Zn. The lower sorption of Cr from multi-metal than single metal model could be explained by competition for sorption sites, with Zn and Cu, which had 170 and 8 times higher concentration, respectively. In studies comparing single and competitive metal sorption, Cr was found to be easily exchanged and substituted by other metals such as Cu and Zn (Park et al., 2016; Shah, 2009).

The lack of change of Zn sorption and lower Cu sorption maximum on sewage sludge with increasing pyrolysis temperature could be explained by the increase in P in the sewage sludge biochar. The extremely high concentration of Zn could have precipitated with the increased P in the sewage sludge biochar, suppressing Cu sorption on the same biochar. The decrease in Cu sorption on sewage sludge biochar, with increasing pyrolysis temperature could be due to loss of oxygen-containing functional group such C = O stretching of aldehyde and carbonate ions at 550 and 650°C (Koetlisi and Muchaonyerwa, 2017; Chapter 3). The reason for decline of Zn sorption and no change in Cu sorption on latrine waste with increasing pyrolysis temperature was not clear. However, the pH of the equilibrium solution could have contributed. Other studies reported that adsorption capacity for Cu (II) by biochar was increased with increase in pH from 2.0 to 6.0 especially on Fe and Zn laden biochar (Zhou et al., 2017). However, Qian et al. (2016) reported that biochar produced from rice straw at low pyrolysis temperature (300 and 400°C) showed the higher removal capacity of metals than those at higher pyrolysis temperatures. Zinc sorption may decrease with increase in pyrolysis temperature owing to loss of chemical functional groups that offer site for physical adsorption. Increasing pyrolysis temperature would have formed less reactive biochar rich in condensed C.

Several other studies reported that pyrolysis temperature influences sorption capacities of different biochars (Xu et al., 2013ab; Kim et al., 2013; Qian et al., 2016). For example, Cr (III) removal by low pyrolysis temperature biochar (100 and 300°C) was higher than high pyrolysis temperature (500 and 700°C) (Qian et al., 2016). On the other hand, removal of Cu, Zn, and Cd by 350°C dairy manure biochar was more efficient than 200°C biochar of the same feedstock (Xu et al., 2013). The current study suggested that, at lower pyrolysis temperature, sewage sludge and latrine waste biochar types were more effective than pine-bark biochar, while at higher temperature, sewage sludge was better than latrine waste biochar for sorption of Zn. Bonding energy is a key quantity describing the strength of the interaction of molecules with the surface (Abild-Pedersen et al., 2007). The bonding energy for Zn was higher on pine-bark than on faecal waste derived biochars. The strength of the

binding between a given metal and a surface may vary from reaction site to the other (Benjamin and Leckie, 1981). It may be because each energy represent the contribution made by the bond to the total atomization energy of the concerned molecule (Sanderson, 1976). Hence, at the greater adsorption density (ions/m² specific surface area), the strongest binding site becomes limiting and average binding constant decreases even though the total number of available unoccupied binding site is large (Benjamin and Leckie, 1981). The lower bonding energy constant of Cu for effluent than single metal solution suggested that sorbed Cu could easily be desorbed. On the other hand, the higher coefficient of bonding energy of Cr on for pine-bark biochar than latrine waste and sewage sludge biochar, suggests stronger bonding, possibly minimising the possibility of desorption. This further supported the view that a different sorption mechanism could have been involved. The lower bonding energy constants of Cr for single metal solutions than effluent for all biochar types at 350°C, suggested weaker bonding, associated with easier desorption.

5.5 Conclusions

Biochar type from sewage sludge is 44.5 and 54.3% and latrine waste is 26.2 and 62.2% more effective for Zn from multiple and single metal solution respectively than those from pine-bark. Sewage sludge biochar is also 68.6 and 60.8% and latrine waste is 67.3 and 71.8% more effective for Cu from multiple and single metal solution respectively than those from pine-bark. Low Cr adsorption shows possible increase of Cr into the environment. While in the environment, various forms of non-retained Cr, may be rendered carcinogenic to put many lives at risk. Sorption of Zn, Cu and Cr from multi-metal effluent on latrine waste and sewage sludge biochar declines with increase in pyrolysis temperature. Biochar derived from human faecal waste, especially sewage sludge, pyrolysed at 350°C is a promising sorbent for removal of metal pollutants such as Zn, Cu and Cr from solution. The use of biochar, as a potentially valuable resource for removal of heavy metals from industrial effluents, could alleviate the challenge of stockpiling of human faecal material. Other studies could investigate on the effectiveness of sewage sludge and latrine waste biochar as soil amendments for immobilization heavy metals.

CHAPTER 6: EVALUATION OF SOIL AMENDMENT WITH BIOCHAR FROM SEWAGE SLUDGE ON HEAVY METAL CONCENTRATIONS IN LEACHATES OF APPLIED INDUSTRIAL EFFLUENT: A LEACHING COLUMN STUDY

6.1 Introduction

Industrial activities such as metalliferous mining, smelting and electroplating and land application of resultant effluents and metal-rich sewage sludge have led to increasing heavy metal contents in soil (Pinto et al., 2003; Diawara et al. 2006; Duruibe et al., 2007; Ahluwalia and Goyal, 2007). For example, agricultural land polluted with Cd, Pb, Cu, and Zn reached 20 million hectares in China, with metal concentrations surpassing national food-safety standards in more than 10 million tons of foodstuffs (Zhou, 2003). While the metals are naturally occurring in soils systems, the concentrations increase when metal-rich biosolids and industrial effluents are applied. In addition to metals reaching toxic levels through uptake by food plants, leaching could pollute groundwater. Strategies to reduce the potential pollution of groundwater through leaching need to be established.

Amendments of soil with organic materials like animal manure and compost have been found immobilize heavy metals in soil (Walker et al., 2003), possibly due to increase of soil pH (Han et al., 2002; Walker et al., 2004). Carbon-based sorbents have demonstrated as cost-effective in reducing mobility of contaminants, including heavy metals (Buss et al., 2016; Xu et al., 2013; Larsbo et al., 2013). The use of biochar from organic wastes as a potential biosorbent for environmental remediation is gaining attention (Park et al., 2016; Uoyang et al., 2016; Qian et al., 2016). Suitability of biochar in the immobilization of heavy metals has been demonstrated owing to the presence of oxygen-rich functional groups (Puga et al., 2016; Qian et al., 2016). Addition of biochar from organic materials like corn-straw and peanut husks decreases concentrations of available heavy metal, including copper and cadmium, in the soil (Cheng et al., 2016; Li et al. 2016; Shen et al. 2016). Park et al. (2016) reported that sesame straw biochar immobilized lead, cadmium, chromium,

copper and zinc in both mono and multi-metal forms. The effectiveness of biochar as a sorbent of heavy metals depends on characteristics associated with the feedstock.

Pine and oak wood biochar exhibited better sorption properties for As, Cd, and Pb than their corresponding bark based biochar (Mohan et al., 2007). Dairy manure biochar simultaneously removed Pb, Cu, Zn and Cd from aqueous solution and sorption capacity was related to its mineral components such as CO_3^{2-} and PO_4^{3-} (Xu et al., 2013). While significant research has been done with biochar derived from forestry and agricultural wastes, investigations on biochar types derived from human faecal wastes are very limited (Liu et al., 2014). Some attention paid on sewage sludge biochar, considered its fertilizer value from great nutrient elements contents perspective (Yuan et al. 2015). While sewage sludge, may contain heavy metals, originating from industrial effluents, large quantities of sludge produced by small municipalities contain low concentrations of heavy metals. High contents of ash, P and pH in biochar from latrine waste and sewage sludge (Koetlisi and Muchaonyerwa, 2017) supports precipitation of heavy metals. Biochar derived from the ubiquitous low metal sewage sludge could have potential for the immobilizing heavy metals.

Based on sorption studies in Chapters 3, 4 and 5, biochar from pyrolysis latrine waste and sewage sludge have potential to immobilize heavy metals. Biochar from latrine waste and sewage sludge (Koetlisi and Muchaonyerwa, 2017) sorbed more Cd than pine-bark based biochar (Koetlisi and Muchaonyerwa, 2018). The results in Chapter 5 also showed that faecal waste biochar has greater potential to sorb Zn and Cu from effluent with multiple heavy metals and from single metal solutions than pine-bark biochar. The higher ash, P and pH in faecal waste biochar could support precipitation of the metals (Xu et al., 2013). The greater effectiveness of faecal waste biochar, than pine-bark biochar, suggests that there is potential for the biochar to reduce mobility and leaching of metals added through land application of effluent in amended soil. Leaching tube studies are essential in understanding these effects at least in the short term. The objective of this study was to determine the effect of rate of sewage sludge biochar on immobilization of heavy metals in a sandy loam soil treated with electroplating industrial effluent under leaching tube conditions.

6.2 Materials and Methods

6.2.1 Soil used in the study

A loam soil was collected from the 0-20 cm depth of the Indian Ocean coastal plain (29°57'24.066"S, 30°55'51.7188"E). The soil was air-dried and sieved (< 2mm) prior to use. The soil had 71.4% sand, 6.0% silt, 22.6% clay, 0.86% OM and pH 7.13 (KCL).

6.2.2 Biochar and effluent used in the study

Sewage sludge biochar, pyrolysed at 350°C, was used in this study based on its superiority in multi-metal sorption batch experiments for sorption of Zn, Cu and Cr. The characteristics of the biochar are presented in Section 3.2.1. Characteristics of the effluent are indicated in Section 5.2.2. Concentrations of Zn, Cu and Cr were above maximum permissible limits for disposal into the environment.

6.2.3 Leaching (Column) Study

The study was conducted following the protocol used by Bame et al. (2013). Columns with 5.3 cm inner diameter and 20 cm long were made with polyvinyl chloride (PVC) pipes. A perforated perspex disc of 22.06 cm² area, overlaid with fine glass fibre mesh, was fitted at the base of each column, to avoid loss of soil-biochar mixture during the study. The biochar treatments were equivalents of 0, 50, and 100 t ha⁻¹ replicated three times. These rates were based on mass of soil in the 0 - 20 cm depth of 1 ha with a bulk density of 1400 kg m⁻³. The columns were filled with soil-biochars mixtures to about 18 cm through light tapping on the bench to pack them evenly to a bulk density of 1460 kg m⁻³ and tight to avoid preferential flow paths. The pore volume was calculated to be 168 ml. Finest glass fibre mesh was placed on soil biochar mixture surface to restrict disturbance by splashing when applying effluent.

The soil biochar mixtures were then leached with industrial effluent weekly for eight weeks. Another set was leached with distilled water. Leaching of biochar for two

weeks is sufficient to achieve leaching equilibria, including sorption-desorption, of all organic and inorganic species (Gao et al., 2014). Each leaching event constituted of an addition of small amounts of effluent or distilled water. Initially, 168 mL (1 pore volume) was added and thereafter leaching was done with 100 mL (0.6 pore volumes) at each event. The pore volumes used were therefore 1, 1.6, 2.2, 2.8, 3.4, 4.0, 4.6 and 5.2. The columns were allowed to drain to allow for the reactions between leaching events. The 100 ml (0.6 pore volume) used for subsequent leaching, on a weekly basis, was because the tubes did not dry out significantly in between leaching events, and as such, enough leachate for analysis was collected. Leachates were analysed for pH, EC, Cr, Cu and Zn. At the end of the experiment, soil biochar mixtures were pushed out of the column, sliced into three equal sections (top, middle and bottom), before air-drying and analysis for pH, EC, and total Cu and Zn.

6.2.4 Statistical Analysis

For different leaching events, data were subjected to analysis of variance (ANOVA) using Stata ® 13.1 (StataCorp, 1985 – 2013). The student t-test at 95% confidence level was used to determine differences between treatment means.

6.3. Results

6.3.1 Leachate volumes as a percentage of added effluent or water

The proportions of leachates collected relative to effluent or water added are presented in Figure 6.1. On the first leaching event, only about 20% of the effluent or water was recovered as leachate. The second event resulted in about 80% leachate recovered, which only slightly increased in subsequent leaching events. Differences in biochar treatments were minimal except for the third and fourth leaching events with effluent (Figure 6.1a) and for the fourth, fifth and sixth with water (Figure 6.1b), where the control (no biochar) had lower proportion of leachate.

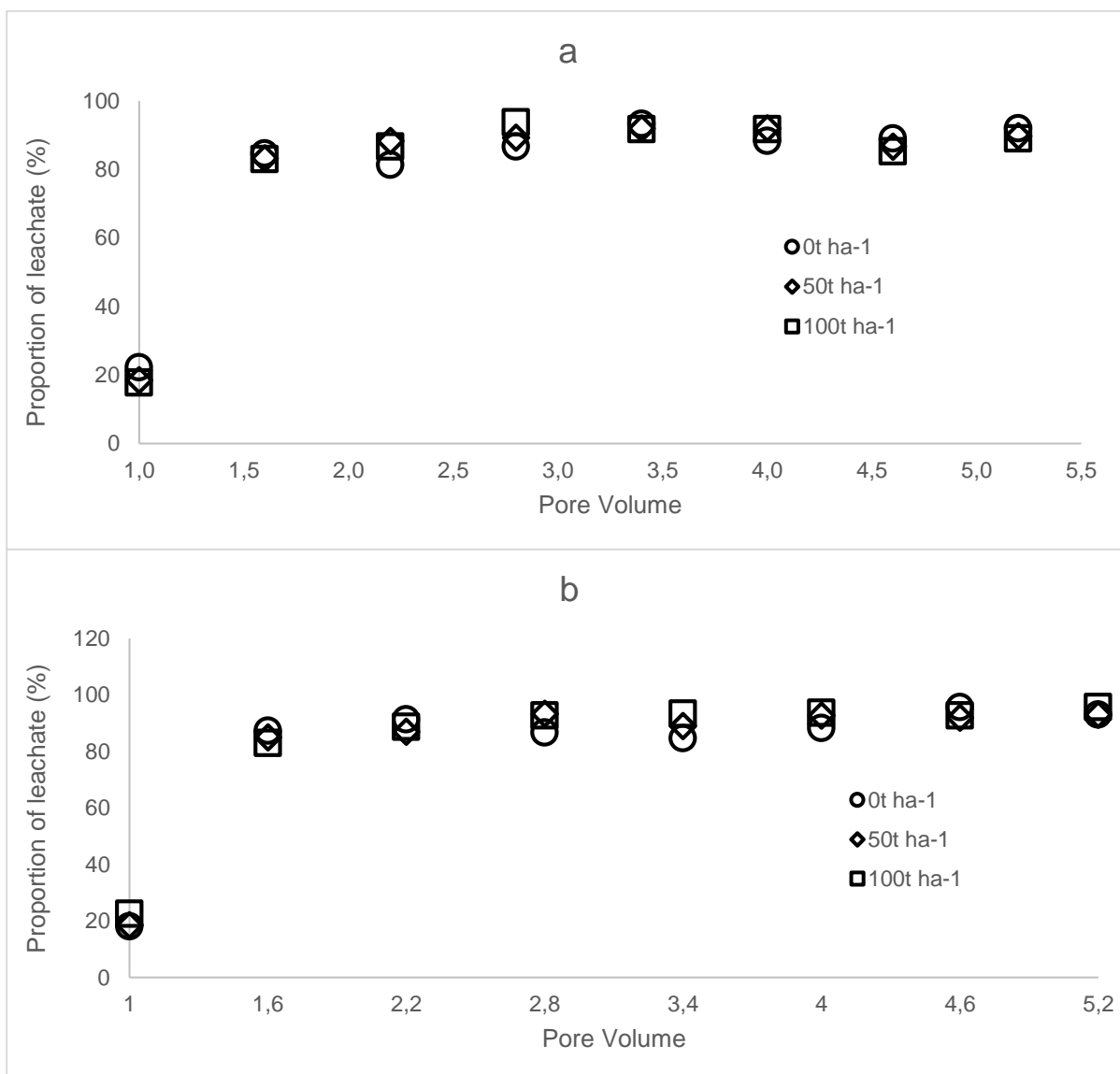


Figure 6. 1: Leachate collected as a percentage of amount of (a) effluent and (b) water applied

6.3.2 pH and electrical conductivity of leachates

Figure 6.2 shows the changes in pH of leachate from soil biochar mixtures throughout study. The initial pH values were between pH 6 and 7. Where effluent was used, leachate pH remained constant for the first four leaching events. From the fifth event leachate pH dropped from pH 7.1 to 3.6 for the control (no biochar), and from pH 6.6

to 4.0 for the 50 and 100 t ha⁻¹ biochar rates (Figure 6.2a). Leachate pH from the control was higher in the first four leaching events, and lower in the last four, than the columns with biochar, where the 100 t ha⁻¹ rate had higher pH than the 50 t ha⁻¹ (Figure 6.2a). Where distilled water was used, leachate pH ranged 6.5 - 8.4 throughout the leaching events (Figure 6.2b). The pH results were generally in the order control > 50t ha⁻¹ > 100 t ha⁻¹ throughout the study. There was a general increase in pH throughout the leaching events for all three treatments, except the 100 t ha⁻¹ rate for which leachate pH declined for the sixth leaching event.

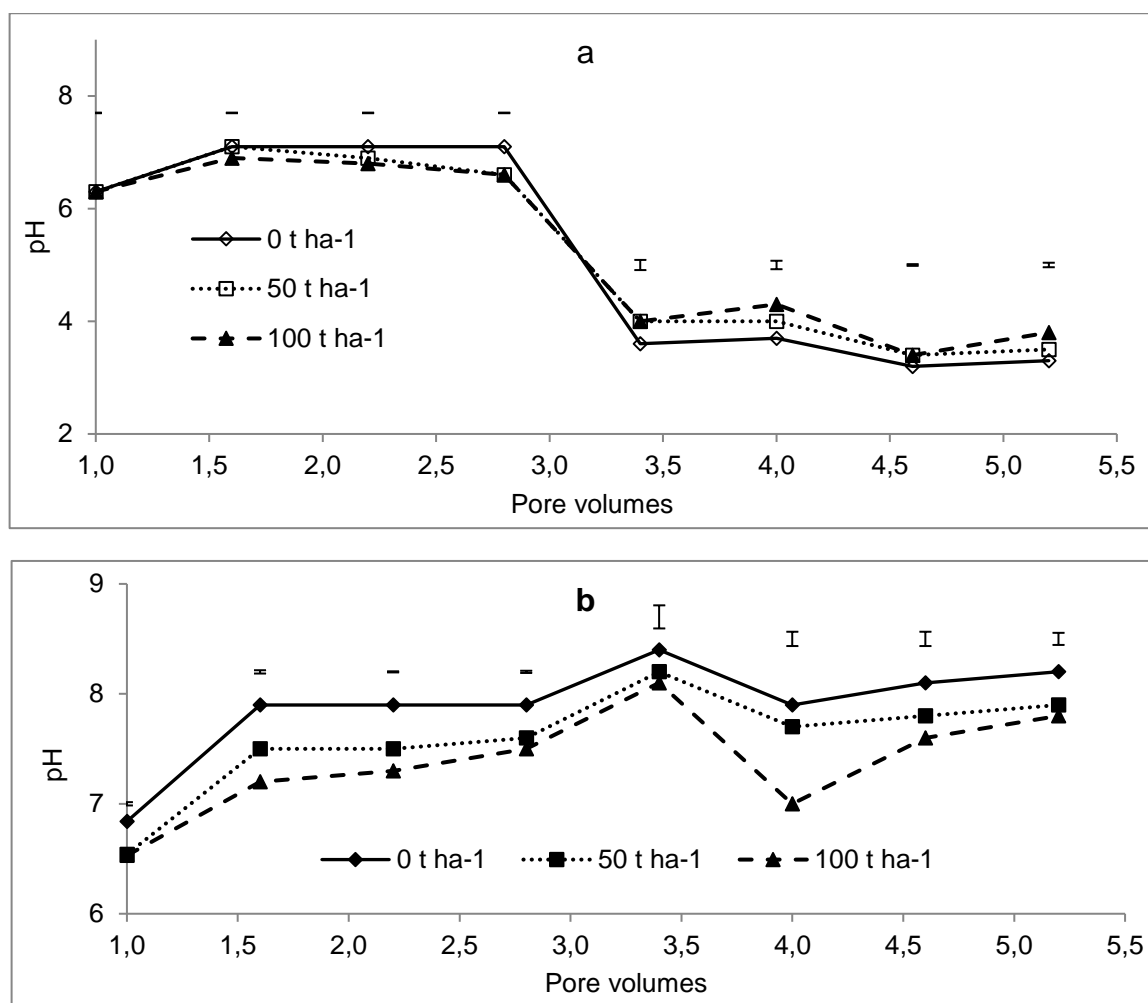


Figure 6. 2: Changes in pH of the leachate from soil treated with sewage sludge biochar and leached with (a) effluent and (b) water. Error bars in the graphs indicate statistical significant difference

Changes in EC with pore volumes are shown in Figure 6.3 (a) effluent and (b) water. The EC values within four weeks with effluent were mostly similar and constant and ranging 10.7 - 12.1 mS cm⁻¹ with the highest on 6th leaching event (43.3 mS cm⁻¹). From week four, EC values increased till week six and decline thereafter. In most occasions, 100 t ha⁻¹ showed higher EC values. Statistical comparisons indicate that 0 t ha⁻¹ had significantly lower (< 0.05) EC than the 50 and 100 t ha⁻¹ at the fifth and sixth leaching events. The leachate EC of treatments leached with water decreased with decreasing rate of biochar throughout the experiment.

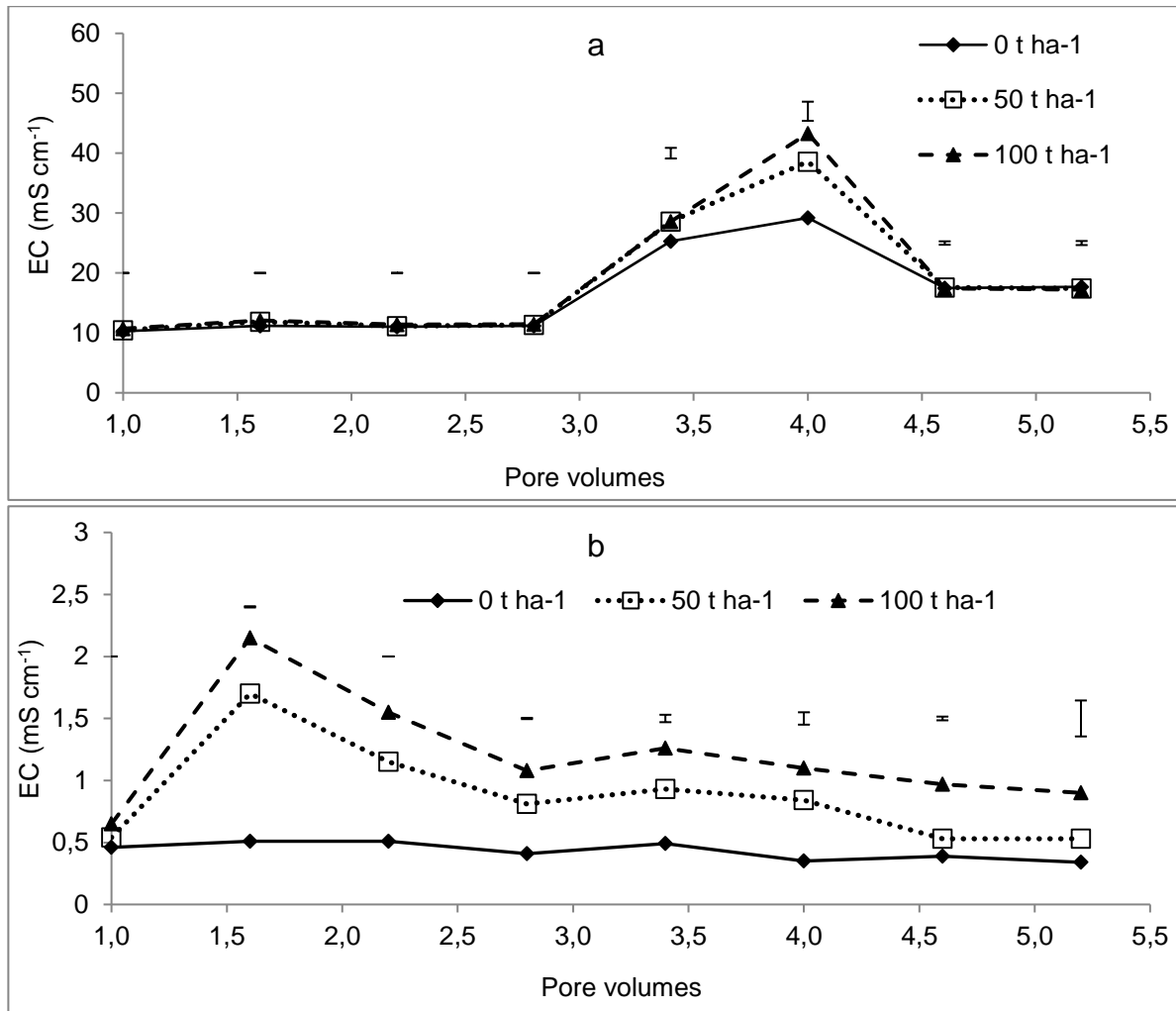


Figure 6. 3: Changes in electrical conductivity of the leachate from soil treated with sewage sludge biochar and leached with (a) effluent and (b) water. Error bars in the graphs indicate statistical significant difference

6.3.3 Concentration of Zn, Cu and Cr in leachates

Zinc was not detectable in all leachates where water was used. Where effluent was used, leachate Zn concentration was not detectable up to the fourth leaching event, increased up to the sixth event and declined thereafter only in the control (Figure 6.4). Leachate Zn concentration was in the order control > 50 t ha⁻¹ > 100 t ha⁻¹ in the fifth and sixth leaching events and the trend reversed for events 7 and 8.

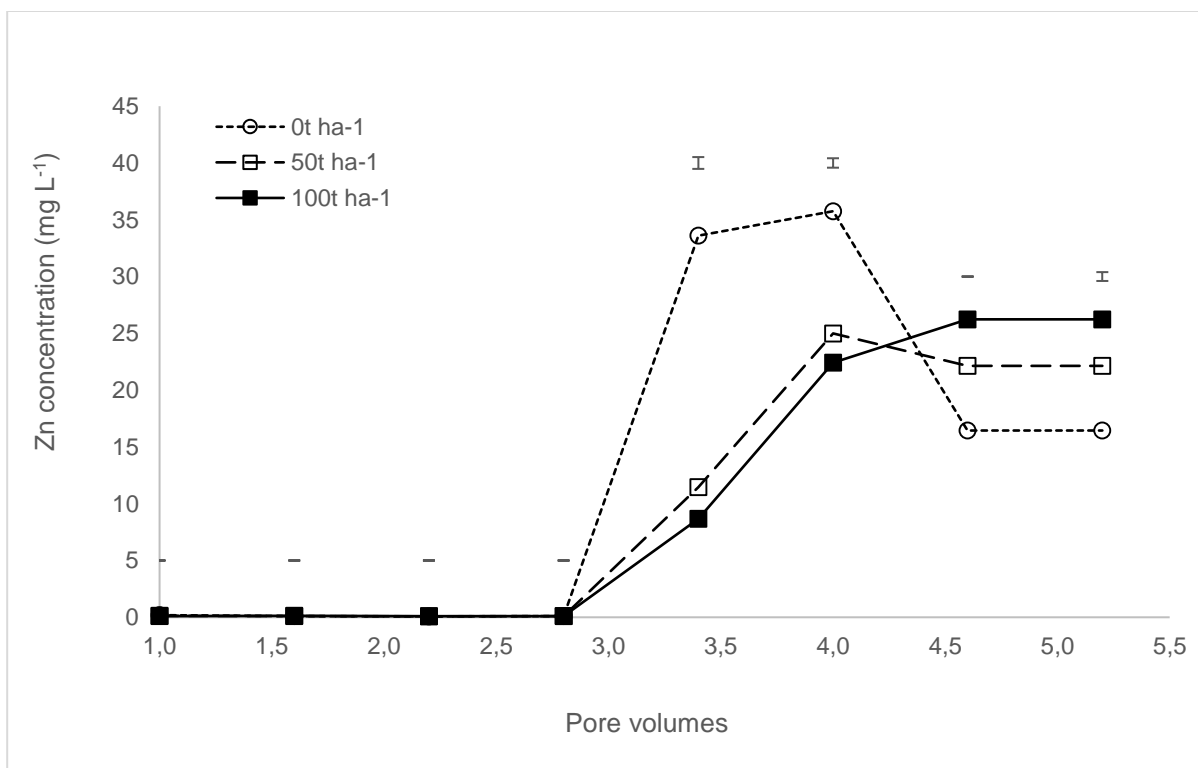


Figure 6. 4: Changes of zinc concentrations in leachate from soil treated with sewage sludge biochar and leached with effluent. Error bars in the graphs indicate statistical significant difference

Copper in the initial leachate was barely detectable and became undetectable up to the fifth leaching event for both effluent and water (Figures 6.5 a, b). The sixth, seventh and eighth events with effluent resulted in significantly higher leachate Cu in

the control (no biochar) and was barely detectable in biochar treatments (Figure 6.5a).

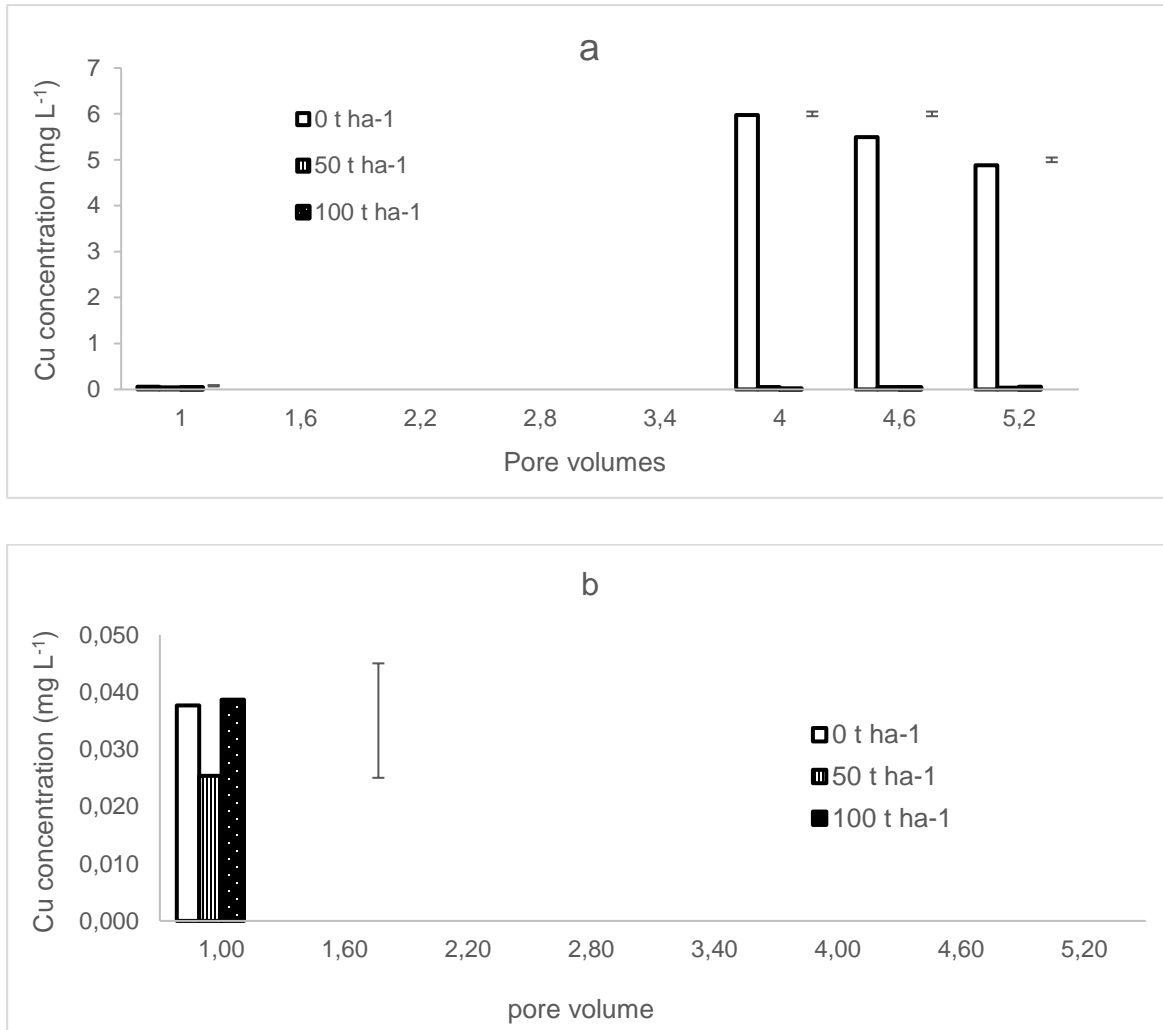


Figure 6. 5: Changes of copper concentrations in leachate from soil treated with sewage sludge biochar and leached with (a) effluent and (b) water. Error bars in the graphs indicate statistical significant difference

Leachate Cr concentration increased with leaching events in the first four events followed by a rapid decline in the fifth leaching event both for effluent (Figure 6.6a) and water (Figure 6.6b). There were no significant differences between biochar rates, and the levels of magnitude were the similar for effluent and water in most leaching

events. In treatments leached with water (Figure 6.6 b), 0 t ha⁻¹ was statistically different from 50 and 100 t ha⁻¹ at the second, third and fourth leaching events.

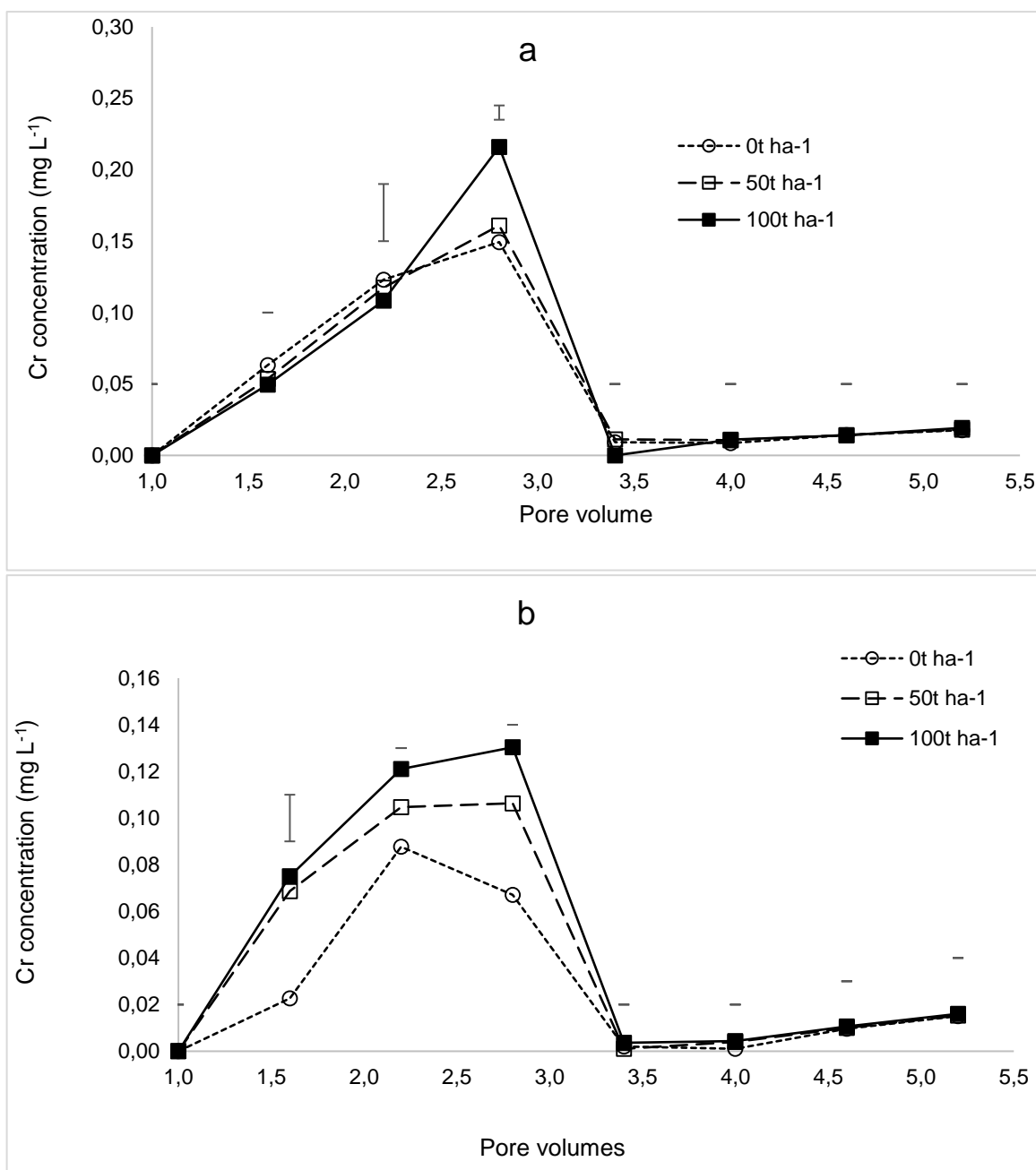


Figure 6. 6: Changes of chromium concentrations in leachate from soil treated with sewage sludge biochar and leached with (a) effluent and (b) water. Error bars in the graphs indicate statistical significant difference

6.3.4 Changes of phosphorus concentrations during the study

Phosphorus release trends were similar for each biochar application rate. There was a general decline in leachate P within the first leaching events followed by a major increase on the forth (further increase for 100 t ha⁻¹ with water), after which the concentration declined. From both leaching with effluent and water, the 100t ha⁻¹ rate resulted in higher leachate P than 50 t ha⁻¹ and the control throughout the experiment. Concentration of P in the leachates were generally higher where water was used instead of effluent (Figure 6.7), for all biochar rates, throughout the study. For example, the highest leachate P concentration for the 100 t ha⁻¹ biochar rate was 54 mg L⁻¹ for effluent (forth leaching event) and 120.3 mg L⁻¹ for water (fifth leaching event). Leachate P in the control treated with water and 50 t ha⁻¹ rate treated with effluent were not statistically significant whereas the rest of the treatments were significantly different in the second leaching event. On the third leaching event, both water and effluent's control and 50 t ha⁻¹ treatments were not significantly different. A similar trend was recorded on the seventh leaching event.

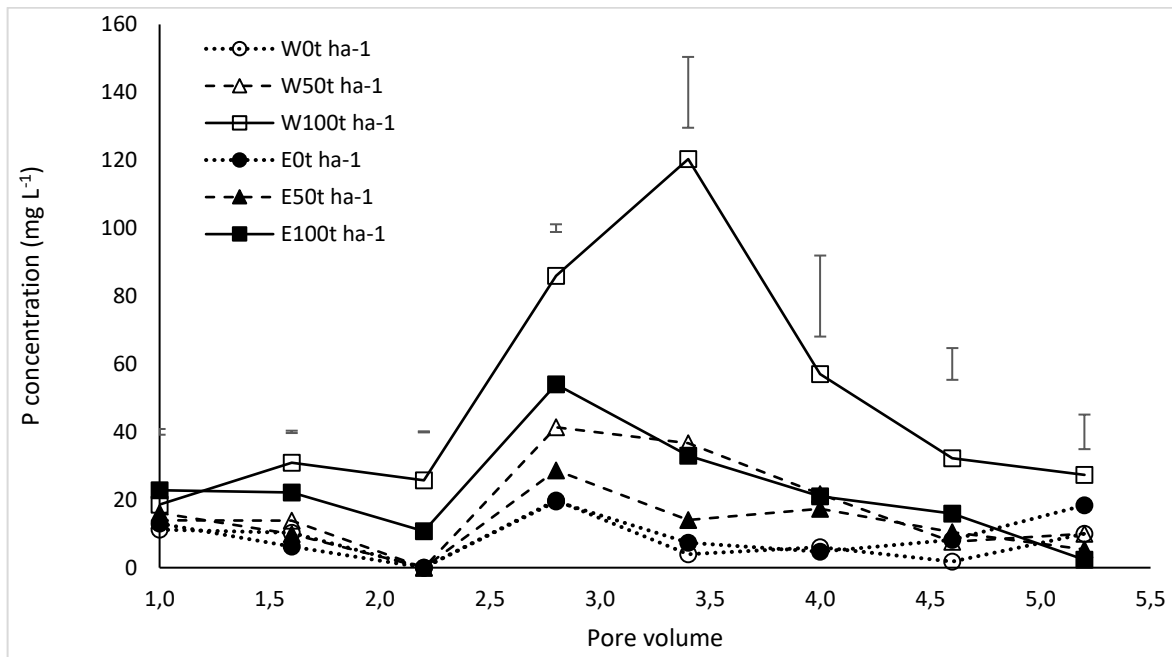


Figure 6.7: Changes of phosphorus concentrations in leachate from soil treated with sewage sludge biochar and leached with effluent and water.

6.3.5 Total zinc and copper in different portions of column soil

Total soil Zn increased with depth in the column but effect of biochar rate was insignificant. Total Zn in the lower section was significantly higher than the top section (Table 6.1). Although biochar rate did not have significant effects ($p>0.05$), the general trend showed an increase with increasing rate for the top and middle sections, while control had slightly higher Zn than other rates in the lower section.

Interaction effect of biochar rate and column position was significant for total soil Cu (Table 6.1). While there were no significant column position effects for the control and the 100 t ha⁻¹ rate, the middle section had higher Cu than the top and the lower sections at the 50 t ha⁻¹ biochar rate. All other treatments had statistically similar levels of total soil Cu.

Table 6. 1: Distribution of Zn and Cu immobilized in different sections of the column leached with effluent

Biochar rate (t ha ⁻¹)	Total soil concentration (mg kg ⁻¹)		
	Upper	Middle	Lower
Zinc*			
0	255	302	545
50	271	356	454
100	430	458	486
Copper*			
0	33.6ab	36.6ab	35.5ab
50	23.7a	54.7b	28.1a
100	43.5ab	46.9ab	46.4ab

6.3.6 Zinc and copper balance after leaching study

The effluent contributed 92, 90 and 88% of the Zn added to the columns with biochar at 0, 50 and 100 t ha⁻¹ rates, respectively. The biochar contributed about 2 and 4% at the 50 and 100 t ha⁻¹ rates, respectively, and the rest (about 8%) was added as part of the soil. As a percentage of total Zn recovered, the soil retained 95% in the control and 97% in the 100 t ha⁻¹ rate. However, some of the Zn added could not be accounted for. Of the Cu added, the effluent contributed 63, 61 and 58% to the soil with biochar at 0, 50 and 100 t ha⁻¹ rates, respectively. Biochar contributed 4 and 8% for the 50 and 100 t ha⁻¹ rate. The soil contributed 37, 35 and 34% of the total Cu added to the columns when amended with biochar at 0, 50 and 100 t ha⁻¹. As a percentage of total Cu recovered, the soil retained 92% in the control and 100% in the 100 t ha⁻¹ rate. Slightly more Cu was recovered than was added in some treatments.

Table 6. 2: Elemental balance of zinc and copper in milligrams (mg) after the leaching of soil amended with sewage sludge biochar and leached with industrial effluent.

Biochar rate (t ha ⁻¹)	Added in soil	Added in biochar	Added in solution	Total added	Recovered in leachate	Recovered in soil	Total recovered	Balance
Zinc								
0	21.0	0.00	234	255	9.30	185	194	61
50	21.0	4.80	234	260	7.28	181	188	72
100	21.0	9.59	234	265	7.45	231	238	27
Copper								
0	6.54	0.00	11.2	17.7	1.47	17.7	19.2	-1.5
50	6.54	0.78	11.2	18.5	0.014	17.9	17.9	0.6
100	6.54	1.55	11.2	19.3	0.011	23.0	23.0	-3.7

No statistical inferences made, but only calculations revealing the ability to recover metals that were added to the medium.

6.4. Discussion

The low leachate as a proportion of effluent or water added at the beginning of the study was because most of the water wetted the soil (Figure 6.1). Subsequent leaching events recovered 80-90% of the effluent or water added because the soil in the column was already moist, with some of the pores occupied by water throughout the experiment. The significant decline in leachate pH (Figure 6.2) between leaching events four and five could be explained by the pH of the effluent, which was pH 2.5. The high pH of the soil buffered the system such that the leachate pH remained close to neutral for four leaching events until all basicity in the system was neutralized (Stumpe and Vlek, 1991) and the pH then became dominated by that of the effluent added. The biochar further buffered the system as shown by lower pH (biochar had pH 6) in the first four leaching events, and higher in the last four leaching events, when compared with the control. These trends in pH could explain the leachate concentrations of Zn and Cu. Masto et al. (2013) reported that availability of metals such as Zn, Cu, and Cd were decreased by application of biochar from both animal and plant wastes.

The generally increasing pH with number of leaching events, where water was used, explains the leachate Cu and Zn, which were below detection, possibly due to precipitation of these metals. The decline in pH beyond four leaching events explains the high leachate Zn and Cu where effluent was used. Zinc and Cu are known to precipitate at high pH levels (Aziz, Adlan and Ariffin, 2008). The precipitation could be as a result of carbonates in the ash of the biochar. Copper and Zn solubility increases at lower pH ranging from 3.2 to 4.3 and decreases at higher pH (Rieuwerts et al., 1998). The high concentrations of Zn (and Cu in the control) explain the high electrical conductivity beyond four leaching events. The pH moderation due to the biochar, together with possible reactions with phosphorus from the biochar, explains the lower leachate Zn for the fourth and fifth leaching event and lower Cu, than the control. While leachate P was highest in the fourth leaching event, its decline could be a result of precipitation with Zn and Cu, which remained soluble due to the low pH

of the leachate. Although low pH would have kept Cu soluble, leachate Cu levels were not detectable in the treatments with biochar.

The high leachate P (Figure 6.7) and non-detectable Cu levels, especially where the pH declined, suggested that the presence of any soluble Cu could have precipitated as phosphates. Available literature indicates that phosphates facilitate precipitation of micronutrient cations such as Zn and Cu (Wei et al., 2006). The contribution of P in the precipitation of the metals is supported by the lower leachate P where effluent was used instead of water. This effect indicated that some of the P from the biochar reacted with the metals in the effluent resulting in lower levels of P in the leachate compared to where water was used. Initially, the metals could have precipitated with carbonates and phosphates in the biochar, and later with phosphates only as pH declined. Although the effect of biochar rate on leachate Zn was the same for leaching events seven and eight, that of leaching event 8 can be explained by higher leachate P in the control than the biochar treatments, while those of leaching event 7 cannot be clearly explained. While the general trends of total soil Zn and Cu supported the view that precipitation occurred as a result of biochar addition, the effects on total Zn and Cu (including precipitates), at the end of the column study, were not significant.

The insignificant effects of biochar rate on total soil Cu and Zn could be because of the dominance of pH of the soil and the effluent. The soil used in this study had a neutral pH, which could have been more important for sorption at the initial stages than the biochar. On the other hand, the highly acidic effluent influenced the pH in the latter stages of the experiment, minimizing the effects of the biochar. The use of an acidic soil and less acidic effluent could have pronounced the biochar effects.

Although the concentrations of Cr (Figure 6.6) measured in the leachate was low, the trend was the same whether effluent or water was used, indicating a greater response to the soil and the treatment and less of the effect of the effluent. The Cr in the leachate was higher in the initial stages of leaching, where P was low, and when leachate Cr declined, leachate P increased, which suggested that the P lowered Cr until soluble Cr got exhausted through leaching. This is in agreement with results

reported by Chowdhury and Yanful (2010). It was reported that as phosphate concentration increases, Cr removal declined (Chowdhury and Yanful, 2010).

As a percentage of total Zn recovered as shown in Table 6.2, the soil retained 95% in the control and 97% in the 100 t ha⁻¹ rate. The higher retention of Zn and Cu at higher biochar rate shows that biochar can retain these elements and reduce the risk of leaching to groundwater. On the other hand, the soil used in this study made greater contribution in retaining Zn and Cu than the biochar, because of its high pH. The high retention in the soil with biochar indicates that the risk of Zn and Cu leaching to groundwater is minimal for this soil and the effect, particularly for Cu, is enhanced by addition of biochar. However, mobility of metals in biochar-amended soil irrigated with effluent needs to be monitored as decline in pH increases mobility, as shown beyond four leaching events with effluent. The portion of the Zn added that could not be accounted for could be because some Zn in the leachate could have been retained when it was filtered before analysis. This effect was higher for Zn than Cu due to the relative concentration of Zn (212 mg L⁻¹), which was more than 20 times higher than Cu (10.2 mg L⁻¹) in the original effluent.

6.5. Conclusions

A loam soil with neutral pH limits the leaching of Zn and Cu from industrial effluent. On the other hand, high pH and soluble P in the biochar could facilitate retention of the metals, however, sewage sludge biochar had no significant effect on Cu and Zn immobilization in the neutral, loam soil, even when applied at extremely high application rates of 100 t ha⁻¹. Low biochar application rate results in higher accumulation of Zn and Cu in the lower section of the leaching column. Biochar immobilization capacity was exhausted on or before the fourth leaching event for all the elements tested. Future research needs to focus on the effects of amendment of different soils with sewage sludge biochar on yield and metal composition of crops irrigation with diluted effluent.

CHAPTER 7: DRY MATTER AND TISSUE COPPER AND ZINC OF SPINACH GROWN ON A LOAM SOIL AMENDED WITH SEWAGE SLUDGE AND LATRINE WASTE BIOCHAR AND IRRIGATED WITH INDUSTRIAL EFFLUENT AND TAP WATER

7.1 Introduction

The increasing demands for water justifies the use of wastewater in irrigation, which frees up freshwater for other primary uses (Madungwe and Sakuringwa, 2007). However, the use of industrial effluents may pose environmental challenges, depending on the chemical composition (Al-Hamaiedeh and Bino, 2010; Ranade and Bhandari, 2014). Industrial effluents originating from electroplating, steel-works, automobile, battery and semiconductor industries may contain heavy metals such as chromium (Cr), cadmium (Cd), copper (Cu) and zinc (Zn) (Doble and Kumar, 2005). For example, effluent from battery factory in Ankara, Turkey, had 0.027 mg Cu L⁻¹ and 0.373 mg Cr L⁻¹ (Bahadir et al., 2007). Treated wastewater in Peri-urban region in Titagarh, India was found to contain 0.01, 0.04, 0.98 and 1.17 mg L⁻¹ of Cd, Cr, Cu and Zn, respectively (Kiziloglu et al., 2008), while wastewater from Cu plating industry in Tamil Nadu, India had 126 mg Cu L⁻¹ amongst other metals (Kadirvelu et al., 2001). Reuse of such wastewater could pose a threat to the environment and human health, through the soil-plant continuum (Fatta-kassinou et al., 2016). Soil properties affect the distribution and mobility of the pollutants, with effects on their uptake by plants and leaching to groundwater.

Some metals are phytotoxic while others are toxic to humans and animals (Nagajyoti et al., 2010). High concentration of metals like Zn and Cu could negatively affect plant growth (Ra et al., 2016). Based on WHO thresholds, high composition of the metals in tissue of vegetables that are irrigated with metal-rich wastewater may pose a risk to human life (Li et al., 2016; Muchuweti et al., 2006). While treatment of wastewater at source could reduce these environmental risks (Zhou et al., 2016), the high costs of treatment (Massoud et al., 2009) makes direct application without treatment the

most common practice. However, there is need to modify the soil environment to reduce mobility and uptake of these metals by crops (Park et al., 2016; Xu et al., 2013). The incorporation of biochar in the soil could reduce the mobility of the metals, depending on characteristics of the biochar. Feedstock types, carbonization conditions and soil type can influence the effectiveness of biochar in soil (Mukherjee and Lal, 2014).

Biochar has been found to adsorb contaminants, including heavy metals, on its surface and reduce mobility (Uchimiya et al., 2010; Beesley et al., 2011; Larsbo et al., 2013; Ogbonnaya and Semple, 2013). Addition of prune residues biochar to mine tailings was reported to reduce bioavailability and leachability of Cd, Pb, Ti and Zn (Fellet et al., 2011). The immobilization of heavy metals by ramie stick biochar has been found to reduce heavy metal content in plant (Shen et al., 2016). Results in Chapters 3, 4 and 5 show that human faecal waste biochar immobilize heavy metals such as Cd, Zn and Cu, from solutions, and this effect may be important in soil.

Chapter 3 in this thesis (and Koetlisi and Muchaonyerwa, 2017) showed that latrine waste biochar had greater ash content, surface area, pore volume and Cd sorption capacity than biochar from sewage sludge. In that study, the sorption capacity ranged from 167 to 250 mg kg⁻¹ for latrine waste and 35 to 143 mg kg⁻¹ for sewage sludge biochar. Results in Chapter 5 showed that biochar from sewage sludge and latrine waste produced at 350°C sorbed up to 400 mg Zn kg⁻¹ and 102 mg Cu kg⁻¹, from an industrial effluent. However, when single metal solutions were used, Zn sorption was lower, while Cu sorption was slightly higher than when effluent was used. The findings suggest that possible reduction in mobility of Zn and increase mobility of Cu could occur, with significant implications on uptake of the two metals when effluent with higher Zn than Cu is used for irrigation. However, where crops are irrigated with freshwater, biochar from faecal waste could contribute phosphorus and micronutrients and increase their availability in the soil. Biochar could also reduce soil bulk density and enhance water holding capacity and availability (Chen et al., 2010; Dumroese et al., 2011; Jien and Wang, 2013; (Baronti et al., 2014).

These possible positive effects suggest that production of biochar, and use as a soil amendment, could be viable waste management strategy for the large volumes of sewage sludge and faecal waste from ventilated and improved pit latrines in parts of KwaZulu-Natal. The biochar could improve the productivity of soils through immobilization of pollutants, where crops are irrigated with wastewater, contributing micronutrients and improving the soil condition. However, effects of amending soil with biochar from sewage sludge and latrine waste on growth and metal uptake of crops irrigated with industrial effluent and freshwater are not clearly understood. The objective of this study was to determine the effects of faecal biochar type on biomass production and heavy metal composition of spinach tissue irrigated with dilute industrial effluent and tap water.

7.2. Materials and Methods

7.2.1 Soil, biochar and effluent used in this study

The soil used in Chapter 6 was also used in this study. Two biochar types derived from sewage sludge and latrine waste, and pyrolysed at 350°C, were used in this study. The details of production and characteristics of the biochar are in Chapter 3. The industrial effluent used in Chapters 5 and 6, was also used in this study. The characteristics are detailed in Chapter 5. The concentrations of Zn and Cu in the effluent were too high for survival of plants. The effluent was, therefore, diluted to 25% of the original concentration before use for irrigation.

7.2.2 Pot trials

A pot experiment was conducted under glasshouse conditions at the School of Agriculture, Earth and Environmental Sciences, University of KwaZulu-Natal. The glasshouse temperature was maintained between 25°C, during the day, and 16°C at night. Three (3) L pots were filled with 2 kg soil, which was then amended with biochar

from (i) sewage sludge or (ii) latrine waste at 0, 17.9, 35.7 and 71.4 g per pot rates equivalent to 0, 25, 50 and 100 t ha⁻¹. These treatments were replicate three times. Inorganic fertilizers were added to the soil/biochar mixtures to provide balanced nutrient requirements according to spinach nitrogen, phosphorus and potassium (NPK) recommendations. Nitrogen, P and K were applied at rates equivalent to 100, 100 and 335 kg ha⁻¹, respectively, using urea (NH₂CONH₂), potassium dihydrogen orthophosphate (KH₂PO₄) and potassium nitrate (KNO₃). Soil moisture was adjusted to achieve the available water capacity of the soil, with dilute effluent (25% of original concentration). Two seedlings (65 day old) of the Ford-hook giant cultivar of spinach (*Spinacia oleracea*), were transplanted per pot. Moisture correction was done with the dilute effluent when required and the volume added was recorded, during the 8-week period. Weeds were manually uprooted from the pots and incorporated into the soil.

After 8 weeks, shoot biomass was harvested by cutting the plants at 1 cm above the soil surface and rinsed with distilled water. A destructive root harvesting method which involved taking root sample carefully to obtain entire root structure was used and thereafter, roots were rinsed free of soil particles by use of water, and then oven dried to obtain dry mass. The shoot and root biomass was weighed and dried to constant weight at 70°C, and the moisture content of the fresh materials was obtained by difference and expressed as a percentage of fresh weight. The dried shoots were crushed to pass through 250 micrometre, and each plant sample (0.5 g) was digested with aqua-regia (1:1 straight HNO₃ and HCl) on a Mars 6 Digestion System. Digestion was done in three stages; first stage involved ramping to 200°C for 20 min, second stage entailed holding the temperature at 200°C for 25 min and the last stage involved cooling for 15 min. The digests were then analysed for Cr, Cu and Zn using Fast Sequential Atomic Absorption Spectrometer (Model AA280FS) and results were expressed in mg kg⁻¹ (Chen and Ma, 2001; Miller, 1998).

The soil in the pots were air dried, sieved to pass through 2 mm sieve and analyzed of pH, EC, Cu and Zn. The heavy metals were extracted from 2.5 g soil sample with 25 mL of 0.01 M CaCl₂ solution (Khodaverdiloo and Samadi, 2011). The suspensions

were shaken in a constant temperature room (25°C) using reciprocating shaker at 180 rev min⁻¹. The equilibrium solution was separated from the solid by centrifugation at 9440*g for 10 min. The supernatant was filtered through Whatman No. 42 filter paper (Khodaverdiloo and Samadi, 2011), and concentrations of Cu, Cr and Zn in the filtrate were determined by AAS. There was no distinction made between metals absorbed in the roots and those adsorbed on the root surface. A portion of each of the soil samples was digested with aqua regia, before analysis of total Zn and Cu. The pH and electrical conductivity (EC) of the residual soil were determined in H₂O at a solid: solution ratio of 1:2.5 w/v. Soil pH was analysed using PHM 210 standard meter, while EC was measured using CDM 210 conductivity meter, using the same water suspensions used for pH. The experiment, including all the treatments and management and data collection, was repeated with distilled water in place of industrial effluent, for irrigation.

7.2.3 Statistical analysis

The data for each pot trial were subjected to analysis of variance (ANOVA) using Stata® 13.1 (StataCorp, 1985 – 2013). The Turkey-Kramer test was performed at the 5% probability level to determine the significant difference between means (Ireland, 2010; Zhu et al., 2013). Mass balances of Zn and Cu were also determined.

7.3. Results

Dry-matter and water content of shoots and roots of spinach irrigated with tap water

Where spinach was irrigated with tap-water, water content was increased in shoots, and reduced in roots, following addition of sewage sludge biochar, particularly at 50 and 100 t ha⁻¹, when compared to the control (Table 7.1). Latrine waste biochar did

not affect shoot and root water content. Shoot water content ranged 68.8 to 79.0% for sewage sludge biochar and 59.9 to 61.7% for latrine waste biochar. Only the sewage sludge biochar at a rate of 25 t ha⁻¹ had higher shoot dry-matter than the control. Latrine waste biochar at 25 t ha⁻¹ resulted in higher root dry-matter than sewage sludge biochar at 50 and 100 t ha⁻¹. Shoot dry-matter ranged from 13.3 to 14.7 g pot⁻¹, while root dry-matter ranged from 10.3 to 15.7 g pot⁻¹.

Table 7. 1: Biomass production components of spinach grown in soil treated with faecal waste biochar and irrigated with tap water

Treatment	Rate (t ha ⁻¹)	Dry matter (g pot ⁻¹)		Water content (%)	
		Shoot	Root	Shoot	Root
Control		13.3a	13.7ab	60.1a	52.0b
LW	25	13.9ab	15.7b	59.9a	51.5b
	50	14.1ab	11.7ab	62.8ab	52.7b
	100	14.1ab	12.5ab	61.7a	49.4b
SS	25	14.7b	11.7ab	68.8bc	40.1ab
	50	13.8ab	10.6a	71.9cd	27.4a
	100	14.0ab	10.3a	79.0d	34.0a

LW and SS stand for biochar from latrine waste and sewage sludge, respectively.

Zinc and Cu content of shoots and roots of spinach irrigated with tap-water

All rates of sewage sludge biochar and 100 t ha⁻¹ of latrine waste biochar increased shoot Zn and Cu, relative to the control, where tap-water was used (Table 7.2). There were no significant differences of shoot tissue Zn across biochar types, except that sewage sludge biochar at 50 t ha⁻¹ had higher tissue Zn while at 25 t ha⁻¹ it had higher

Cu than latrine waste biochar applied at 25 t ha⁻¹. Sewage sludge biochar did not affect root Zn and Cu compared the control. Latrine waste biochar had higher root Zn at 100 t ha⁻¹ and higher root Cu at 50 and 100 t ha⁻¹ than the control.

Table 7.2: Zinc and Cu concentration in spinach grown in soil treated with faecal waste biochar and irrigated with tap water

Biochar	Rate (t ha ⁻¹)	Tissue Zn (mg kg ⁻¹)		Tissue Cu (mg kg ⁻¹)	
		Shoot	Root	Shoot	Root
Control		nd	nd	nd	nd
LW	25	0.09a	0.09	0.06	0.07a
	50	0.21ab	0.14	0.07	0.64c
	100	0.30ab	0.19	0.08	0.30b
SS	25	0.28ab	0.09	0.13	0.02a
	50	0.32b	0.09	0.13	0.13ab
	100	0.20ab	0.15	0.10	0.15ab

LW and SS stand for latrine waste and sewage sludge biochar. Nd = not detectable.

Soil pH, EC, extractable zinc and copper after spinach irrigated with tap-water

There were no effects of biochar type and rate on EC and extractable Zn (Table 7.3), except sewage sludge at 100 t ha⁻¹ in soil irrigated with tap water, which had higher EC than all other treatments (Table 7.3). However, there was a general decline of extractable Zn with biochar rate, from 473 to 133 mg kg⁻¹ for sewage sludge biochar and from 542 to 263 mg kg⁻¹ for latrine waste biochar. Where tap-water was used, latrine waste biochar resulted in higher soil pH than sewage sludge biochar, at the same rate of 50 t ha⁻¹. Latrine waste biochar at 25 t ha⁻¹ resulted in higher soil pH than sewage sludge biochar at 50 and 100 t ha⁻¹. Extractable soil Zn ranged 1.3 to 4.43 mg kg⁻¹ for sewage sludge biochar while it was below detection limit for latrine

waste biochar, where tap-water was used. Extractable soil Cu concentrations were all below detection limit and not reported.

Table 7. 3: Residual soil pH, EC and Zinc in soil treated with faecal waste biochar and irrigated with tap water

Treatment	Rate (t ha ⁻¹)	pH	EC (µS cm ⁻¹)	Extractable Zn (mg kg ⁻¹)
Control		7.94abc	35.6a	nd
LW	25	8.11c	29.9a	nd
	50	7.99bc	31.2a	nd
	100	7.92abc	42.2a	nd
SS	25	7.91abc	29.7a	3.27
	50	7.74a	42.4a	4.43
	100	7.78ab	73.3b	1.30

LW and SS stand for biochar from latrine waste and sewage sludge, respectively. Nd = not detectable.

Dry-matter and water content of spinach shoots and roots irrigated with effluent

Biochar did not affect water content and dry-matter where spinach was irrigated with effluent (Table 7.4). Shoot dry-matter ranged 12.0 to 13.2 mg pot⁻¹, while shoot water content ranged 50.9 to 60.0%. When compared to the control, sewage sludge biochar reduced root dry-matter (except 50 t ha⁻¹) and root water content, while latrine waste biochar did not have any effects.

Table 7. 4: Biomass production components of spinach grown in soil treated with faecal waste biochar and irrigated dilute industrial effluent

Treatment	Rate (t ha ⁻¹)	Dry-matter (g pot ⁻¹)		Water content (%)	
		Shoot	Root	Shoot	Root
Control		12.0	10.6bc	54.1	37.2b
LW	25	12.0	10.1abc	54.3	33.1b
	50	12.4	10.5bc	55.5	35.2b
	100	13.2	10.7c	60.0	39.7b
SS	25	12.8	9.63a	56.2	13.9a
	50	12.9	9.82ab	56.0	13.8a
	100	12.3	9.53a	50.9	18.3a

Means with different letters in each column are significantly different. LW and SS stand for from latrine waste and sewage sludge biochar.

Zinc and copper in shoot and root tissue of spinach irrigated with effluent

Biochar did not have any effects on shoot Zn, irrespective of rate and type, where the crop was irrigated with effluent. Sewage sludge biochar increased root tissue Zn, when compared with the control, with the concentrations in the order 100 < 50 < 25 t ha⁻¹. Conversely, latrine waste biochar did not have an effect on root tissue Zn, except at 50 t ha⁻¹ where it was higher than the control (Table 7.5). Increasing the biochar rate increased tissue Cu in roots for both biochar types and in shoots for sewage sludge biochar, especially when compared with the control. At all rates, biochar from sewage sludge resulted in higher shoot and root tissue Cu than latrine waste biochar. The concentration of root Cu followed a similar trend to that of Zn. Concentrations of Cu in the roots were more than twice the concentration of Zn.

Soil pH, EC, extractable zinc and copper after spinach irrigated with effluent

There were no effects of biochar type and rate on pH, EC and extractable Zn (Tables 7.6). Extractable soil Cu concentrations were below detection limit.

Table 7. 5: Zinc and Cu concentrations in spinach grown in soil treated with faecal waste biochar and irrigated with industrial effluent

Treatment	Rate (t ha ⁻¹)	Tissue Zn (mg kg ⁻¹)		Tissue Cu (mg kg ⁻¹)	
		Shoot	Root	Shoot	Root
Control		29.8	14.2a	10.0a	50.5a
LW	25	27.0	14.6a	10.5a	54.0b
	50	27.8	16.8b	13.1ab	56.0bc
	100	22.3	14.3a	13.3ab	58.0c
SS	25	30.7	29.6e	26.2c	61.4d
	50	27.8	25.3d	21.9bc	64.5e
	100	36.9	23.4c	24.3c	81.9f

Means with different letters in each column are significantly different. LW and SS stand for biochar from latrine waste and sewage sludge, respectively.

Table 7. 6: Soil pH, EC, extractable zinc and copper in soil treated with faecal waste biochar and irrigated dilute industrial effluent

Treatment	Rate (t ha ⁻¹)	pH	EC (μS cm ⁻¹)	Extractable Zn (mg kg ⁻¹)	Total (mg kg ⁻¹)	
					Zn	Cu
Control		6.86	297	2.48	88.6a	13.9a
LW	25	6.62	293	5.42	*	*
	50	6.67	348	4.14	81.5a	25.6b
	100	6.82	327	2.63	136.2b	25.6b
SS	25	6.77	287	4.73	*	*
	50	6.86	348	1.49	90.7a	22.2ab
	100	6.94	292	1.33	92.2a	22.9ab

LW and SS stand for biochar from latrine waste and sewage sludge, respectively. * not measured.

Elemental balance of zinc and copper in amended soil irrigated with effluent

The elemental balance results of Zn and Cu for soils amended with latrine waste and sewage sludge biochar treated with dilute industrial effluent are presented in Tables 7.7 and 7.8. Zinc added in biochar was higher for latrine waste biochar than in sewage sludge at each biochar rate. The recovered Zn in shoots and roots was greater in sewage sludge than in latrine waste biochar. Zinc retained in the soil at 100 t ha⁻¹ biochar rate is greater than the control and 50 t ha⁻¹ treatments. Zinc retained the soil in 100 t ha⁻¹ latrine waste biochar was greater, resulting in a lower metal balance than for sewage sludge. More Cu was recovered in tissue components of sewage sludge biochar treatments than latrine waste biochar (Table 7.8). In all the treatment biochars, recovered Cu increased relatively with increase in biochar rate. The 100 t ha⁻¹ biochar yielded the highest recovered Cu in plant tissue. Copper retained in the soil with latrine waste biochar at 50 and 100 t ha⁻¹ is greater than for sewage sludge. This was supported by lower tissue Cu recovered in latrine waste biochar treated soil.

Table 7. 7: Mass balance of zinc after effluent irrigation of spinach grown on soil amended with biochar from latrine waste and sewage sludge at 0, 50 and 100 t ha⁻¹.

Biochar (t ha ⁻¹)	Initial soil (mg)	Added in biochar (mg)	Added as effluent (mg)	Total added (mg)	Recovered in shoot and roots (mg)	Retained in soil (mg)	Total recovered (mg)	Balance (mg)
<i>Latrine waste</i>								
0	69.35	0	230.02	299.37	0.994	177.2	178.194	121.18
50	69.35	11.89	230.02	311.26	1.02	163	164.02	147.24
100	69.35	23.8	230.02	323.17	0.87	272.4	273.27	49.90
<i>sewage sludge</i>								
0	69.35	0	230.02	299.37	0.994	177.2	178.194	121.18
50	69.35	10.8	230.02	310.17	1.206	181.4	182.606	127.56
100	69.35	21.6	230.02	320.97	1.316	184.4	185.716	135.25

Table 7. 8: Mass balance of copper after effluent irrigation of spinach grown on soil amended with biochar from latrine waste and sewage sludge at 0, 50 and 100 t ha⁻¹.

Biochar rate (t ha ⁻¹)	Initial soil (mg)	Added in biochar (mg)	Added as effluent (mg)	Total added (mg)	Recovered in shoot and roots (mg)	Retained in soil (mg)	Total recovered (mg)	Balance (mg)
Latrine waste								
0	16.98	0	11.067	28.047	1.376	27.8	29.176	-1.13
50	16.98	1.5	11.067	29.547	1.582	51.2	52.782	-23.24
100	16.98	2.99	11.067	31.037	1.704	51.2	52.904	-21.87
sewage sludge								
0	16.98	0	11.067	28.047	1.367	27.8	29.167	-1.12
50	16.98	0.73	11.067	28.777	1.963	44.4	46.363	-17.59
100	16.98	1.46	11.067	29.507	2.318	45.8	48.118	-18.61

No statistical inferences made, but only calculations revealing the ability to recover metals that were added to the medium.

7.4. Discussion

The lack of response of dry matter yield to biochar addition could be because all the major nutrients were supplied as fertiliser. Some reports in the literature indicate that crop yield may not be affected (Namgay et al., 2010) or may decline (Mukherjee and Lal, 2014) due to biochar application. While dry matter of spinach irrigated with tap water did not respond at 50 and 100 t ha⁻¹ of both biochar types, the increase in tissue Zn at 50 t ha⁻¹ sewage sludge biochar suggested that the nutritional value of the spinach biomass was improved. The concentrations of Zn and Cu in all the treatments irrigated with tap-water were below the maximum permissible limits of 60 mg Zn kg⁻¹, and 40 mg Cu kg⁻¹ for human consumption (Bempah et al., 2012), suggesting that no negative effects of human health would be expected.

Although the water content was not related to shoot dry matter, lower root dry-matter accumulation in the sewage sludge biochar treatments corresponded with lower water content. The higher root dry matter in the treatment with 25 t ha⁻¹ of latrine

waste biochar than 50 and 100 t ha⁻¹ of sewage sludge biochar could be explained by lower water. The higher water content in the shoots, and lower in the roots, of sewage sludge biochar treatments than latrine waste biochar, suggested differences in partitioning of water. The reason for such differences in partitioning of water between the biochar types was not clear. However, the lower water content in roots at 50 and 100 t ha⁻¹ sewage sludge biochar could have caused greater concentration and toxicity of Cu and Zn to spinach in these treatments. The greater water uptake could have resulted in the greater uptake of Cu and Zn, causing higher tissue concentrations. Positive and negative impacts of increased biochar rate on yield have been reported in the literature (Glaser et al., 2002; Jeffery et al., 2011). Kammann et al. (2011) reported that biochar application increased yield of quinoa, but there were no differences between the 100 and 200 t ha⁻¹ rates. The reason for the difference could be associated with differences in crops used and the soil pH (pH 7.1) of the loam (22.6% clay) in the current study and management of the fertilisation. Kammann et al. (2011) applied fertigation using compound fertilizer and micro-nutrient solution. Whereas biochar has liming effects, there was no such effects for the soil with neutral pH. The lack of significant differences soil extractable Zn levels, and the non-detectable soil Cu among the treatments irrigated with water, could be because of exhaustion of available forms through uptake by plants and precipitation due to the near neutral to alkaline pH of the biochar amended soil.

The generally lower shoot and root dry matter levels where effluent was used, in place of tap-water, suggested that the effluent had toxic effects on spinach. Qadir et al. (2010) reported that irrigation with effluent containing various metals including Zn and Cu reduced crop yield. Therefore, soil EC was expected to be high enough to limit water uptake due to osmotic potential, which is supported by the generally lower water content in both shoots and roots, possibly affecting growth. The soil EC was relatively higher where effluent was used compared to tap water. The reduction of root dry matter, in treatments with sewage sludge biochar, was in response accumulations of Cu and to a lower extent, Zn in the roots, which occurred in these treatments. The root tissue composition where effluent was used was generally

higher than where tap-water was used. The toxicity of Cu over Zn on root growth has been reported in many studies on various plants (Wong and Bradshaw 1982). Sewage sludge biochar resulted in greater availability of water (tissue water content) than latrine waste biochar and the control, possibly as a result of a relatively low density of the biochar that lowered bulk density of amended soil, increasing the ability to retain water and hence improving plant available water (Baronti et al. 2014; Laird 2008). Sewage sludge biochar used in the current study had a bulk density of 716 kg m³, while latrine waste biochar had 806 kg m³.

Pedrero et al. (2010) reported accumulation of metals below critical limits for edible plant parts of plants irrigated with treated effluent. Even though Cu and Zn are essential nutrients, elevated concentrations inhibit growth by causing folia interveinal chlorosis for Cu (Reichman 2000) and restricting root cell division and elongation, and causing chlorosis and necrotic lesions for Zn (Rout et al. 2003; Malik et al., 2010). Toxicity of both Zn and Cu leads to reduced growth and biomass production. The guidelines for safety limits of Cu and Zn in most plants are 40 and 60 mg kg⁻¹, respectively (Singh et al., 2010). The effluent used had higher Zn concentrations (53 mg L⁻¹) than the phytotoxicity threshold of 0.1mg L⁻¹. Pandey (2006) reported that plant tissue Zn was higher following irrigation with industrial effluent and that such a challenge could be addressed with the aid of biochar. Li et al. (2016) reported that hardwood biochar reduced Cu uptake in rice tissue and extractable concentration of Cu in soil. Derakhshan et al. (2017) reported that application of biochar reduces plant uptake and accumulation of Zn and Cu on leafy mustard green (*Brassica juncea*). While adsorption and precipitation of Cu and Zn on the soil and biochar could have reduced their concentration in the soil solution, continuous watering with the wastewater resulted in reduction of the sorption sites, over time.

The near neutral pH of the latrine waste biochar, which was almost similar to that of the soil means that the addition of the biochar did not modify pH of the medium overall or locally. Although overall pH of the residual soils was not different among the treatments, the pH around the sewage sludge biochar particles would have been lower than the soil matrix, which results in greater mobility and toxicity of the metals

from the effluent. Soil pH around granules of soil amendment is different between granules and surrounding soil (Black et al., 1986). Black et al. (1986) reported that at each sampling event, the highest pH was recorded 2 - 4mm below the amendment granule. Some studies showed that biochar addition increase soil pH and improved crop production (Shen et al., 2016), while others have reported a decreased in pH (Abujabhah et al., 2016). The pH of the residual soil was generally lower than where tap water was used due to the acidic nature of the effluent used and was in the range where almost all plant essential nutrients are available.

The higher root concentration of Cu and Zn in treatments with sewage sludge biochar was, therefore, a result for greater mobility due to lower pH (pH 5.9) than that of latrine waste biochar (pH 6.9). Rieuwerts et al. (1998) support this argument that precipitation is unlikely to occur in acid conditions, such conditions would rather favour adsorption than precipitation. The lower root dry matter in treatments where sewage sludge was applied than the control, indicated that the biochar increased the toxicity of the metals, possibly as a result of higher mobility of the elements added with the biochar with a pH 6 than 6.9 for latrine waste biochar. Even though the Cu and Zn contents were slightly higher in the latrine waste biochar, the root contents were lower suggesting that it is the modifying effect of the biochar to the soil conditions, and not initial metal contents that affects tissue composition. Mukherjee and Lal (2014) reported that some biochar amendments are capable of aggravating mobility of metals such as Cu. The higher pH resulted in the retention of Zn and Cu in latrine waste biochar in unavailable forms, possibly through precipitation than where sewage sludge biochar was applied. This view is supported by the higher total Cu and Zn retained in the residual soil treated with latrine waste biochar, particularly at 100 t ha^{-1} , than sewage sludge. The general trend of lower soil Zn in the treatments with sewage sludge biochar could also be because of greater uptake (higher tissue concentrations).

Preliminary sorption studies showed that biochar from sewage sludge and latrine waste sorbed high levels of Cu and Zn from the same effluent, including at concentrations higher than that used in this study (Chapter 5). Fellet et al. (2011)

observed decreased bioavailability of Cd and Zn of the mine tailings with increasing biochar rate. The lack of biochar effects, irrespective of type and rate, on pH, EC and extractable Zn of the residual soil after spinach harvest, indicates that the continuous addition of the effluent, reduced sorption sites, nullified effects of biochar, left toxic levels of the metals in mobile form for plant uptake. For example, Zn concentration on latrine waste biochar treatments was 5.42 and 2.63 mg kg⁻¹ for 25 and 100t ha⁻¹ biochar rate. Based on the preliminary sorption experiments the higher Zn than Cu in the effluent could have resulted in higher sorption of Zn at the initial stages of the experiment. Continuous irrigation with the effluent could have resulted in sorption sites being reduced. This view was supported by visual observations on the leaf tissue, on which necrosis and chlorosis was not observed in the early stages up to four weeks, beyond which the symptom started to show. The biochar effects could possibly have been more evident, and the phytotoxic effects reduced if the metal concentration in the effluent was lower, or if the effluent was applied once off or alternated with freshwater. The greater Zn recovered in plants treated with sewage sludge biochar is indicative that latrine waste biochar was capable of retaining more Zn. Furthermore, the significance of more Zn and Cu being retained in the soil-latrine biochar system is important for the biochar for metal immobilization.

7.5. Conclusions

Generally, spinach shoot and root dry matter was lower while tissue Cu and Zn were higher where effluent was used in place of tap-water. Shoot dry matter did not respond, while shoot tissue Cu and Zn were affected by rate of both biochar types when irrigated with tap water. Increasing rate of both sewage sludge and latrine waste biochar types improves the Cu and Zn nutritional value of spinach, where freshwater is used. Sewage sludge biochar lowered root dry matter and water uptake increased root Zn and Cu of spinach irrigated with effluent when compared to latrine waste biochar and the non-amended control. Both biochar types did not affect dry matter,

water content and tissue Zn of the shoots, while sewage sludge biochar significantly increased shoot Cu. Sewage sludge biochar reduces root dry matter by increasing tissue Cu and Zn from industrial effluent, while latrine waste biochar may have no effects. Root Cu increased significantly due to biochar addition when spinach was irrigated with dilute industrial effluent. Root Cu increased by 6.5, 9.8 and 12.9% in latrine water biochar amended neutral soil when biochar was applied at 25, 50 and 100 t ha⁻¹, respectively. Root Cu increase was pronounced to 17.8, 21.7 and 38.9% in sewage sludge when biochar rate was applied at 25, 50 and 100 t ha⁻¹, respectively. Elemental balance show that latrine waste biochar is more effective in immobilization of both Zn and Cu in soil. The artificial conditions existing under glasshouse conditions and repacked soil columns in pots, have had the tendency to manipulate metal uptake comparative to what would be obtained with field conditions. This study was carried out with a neutral soil using acidic effluent with high concentrations of metals. Further studies need to test the effectiveness of these biochar types on a variety of soils, including acidic ones, using effluents with lower metal concentration than used in this study. Alternatively, the studies could alternate effluent and tap water.

CHAPTER 8: GENERAL DISCUSSION, CONCLUSION AND RECOMMENDATIONS

8.1 General discussion

Heavy metals from both industrial and domestic effluents need to be restricted from natural water bodies, and their mobility needs to be reduced when they are introduced to soil through irrigation (Hussain, Maitra, and Ali, 2017). Biochar derived from organic wastes (Eazhilkrishna et al., 2017) has been used as an effective and low-cost adsorbents capable of removing heavy metals from contaminated systems (Alam et al., 2017) and as fertilizer carrier matrix (Kammann et al., 2017). The type of feedstock and pyrolysis condition are essential in determining the characteristics and effectiveness of biochar (Novais et al., 2017; Tan et al., 2015). For example, biochars produced from plant biomass usually have low EC whereas animal manure-derived show the opposite trend (Singh et al., 2010). While biochar from woody feedstock has been tested, limited work has been done on the effectiveness of biochar from human faecal waste. Zhang et al. (2017) reported that biochar from faecal feedstock could present an excellent sorbent for metal retention and immobilization. No research has been done with biochar from latrine waste and sewage sludge relative to wood-based biochar. Pyrolysis of latrine waste and sewage sludge to produce biochar could be a solution for disposal and recycling of a marginal resource, yielding a product without pathogens and has potential fertilizer value. The main objective of this research was to investigate the influence of pyrolysis conditions and feedstock on properties of biochar from sewage sludge, latrine waste and pine-bark and their effectiveness for heavy metals removal from industrial effluents. Another objective was to determine effectiveness of the biochar on reducing mobility of metals in soil treated with effluent.

This study showed that latrine waste had higher biochar yield than biochar types from sewage sludge and pine-bark due to higher ash and lower volatile matter, possibly as a result of longer storage in the pit, before emptying. Degradation of volatile matter derived from lignocellulosic components (Liu et al., 2014), resulted in lower yield. This

view is supported by the decline in yield, volatile matter, total C, N and H and increase in ash content, surface area and porosity, and variation in surface functional groups with pyrolysis temperature. The lower ash and total P content in pine-bark biochar than biochar from latrine waste and sewage sludge were explained by the composition of the feedstocks. While there were no differences in pH between the biochar types produced from the different feedstocks at 550 and 650°C, the pH varied for biochar types produced at 350°C with the order latrine waste > sewage sludge > pine-bark. The higher ash content, surface area, pore volume and pH (at 350°C) supported Cd sorption onto latrine waste biochar.

Carbonates and oxides, in ash, influence heavy metal adsorption and retention (Xu et al., 2013) and the low ash content (Singh *et al.*, 2010) in pine-bark biochar explains the low Cd removal efficiency from solutions. Animal manure-derived biochars produced at low pyrolysis temperature (350°C) was found to be rich phosphate and carbonates which contributed to the biochars' affinity and potential for heavy metal sorption (Xu et al., 2013). Although Cd sorption on pine-bark increased with increase in pyrolysis temperature, its highest sorption value was still lower than those from the faecal waste source.

Biochar from sewage sludge had a slightly higher affinity for Cu from single metal solution than latrine waste biochar, which sorbed more than pine-bark biochar. Findings indicate that human faecal waste derived biochars are capable to sorb more metals especially Cu and Cd (Agrafioti et al., 2013; Liu et al., 2014) compared to plant-derived biochar. This behaviour is associated with ash and fixed C for Cu, ash and pH and total P for Cd. Chen et al. (2011) reported that pH significantly affects the adsorption of Cu and Zn onto biochar. While the trends of Zn sorption from industrial effluent followed the same trend as for Cu, the trend was in the order pine-bark > latrine waste > sewage sludge where single metal solution was used. This trend was similar for Cr both for single metal solution and for industrial effluent. This suggests that a different mechanism was involved. The higher sorption of Zn and Cr follow the trends of surface area and pore volume, suggesting that surface functional groups are more essential. Porous structure, large surface area and surface functional

groups are significant properties of biochar for high removal efficiencies of pollutants (Tan et al., 2015; Aly, 2016; Abdelhafez et al., 2017; Cao et al., 2017). This finding suggests that plant-derived biochar could be more effective in removal of Zn from single metal solution, and Cr both from single metal and multiple metal effluents than biochar from faecal wastes. The higher (at least 8 times) maximum sorption of Cr for single metal solutions than multiple metal effluent for all the biochars, suggested that competition for sorption sites with other metals in the effluent reduced the sorption.

The sorption of Zn increased on biochar from latrine waste and sewage sludge and decreased on pine-bark biochar where effluent was used instead of single metal solution. This followed a reverse trend for Cu, which suggested that similar mechanism was involved between the two metals and that there was competition. The higher concentration of Zn in the effluent resulted in greater competitiveness than Cu, leaving more Cu in solution, while Zn was sorbed. The higher ash (with associated carbonates and oxides), pH and P in the biochar from latrine waste and sewage sludge could have resulted in precipitation of the Cu and Zn, with more precipitation of Zn due to concentration effects. Chen et al. (2011) reported that pH significantly affects the adsorption of Cu and Zn onto biochar. The results of metal sorption explain the concentrations of Cu and Zn in the leachates from the leaching tube study.

Higher biochar rate on the leaching study resulted in higher retention of Cu and Zn, and lower leachate concentrations, especially in the early stages. In the leaching study, the difference in metal concentration between the control (no biochar) and 100 t ha⁻¹ rate gives an indication and evidence of sorption efficacy of the used biochars. The available literature indicates that mobility of Zn, Cu and Cd is decreased by biochar addition (Mohan et al., 2014; Masto et al., 2013; Inyang et al., 2012). The non-detectable concentration of Cu and Zn in the leachates up to four leaching events is an indication of complete sorption of the metals. Since the control also had low Zn and Cu in the leachate, the contribution of the soil used is important and is explained by the neutral pH. While no measurable Cu was observed in leachate of biochar-amended soil, significant concentrations were measured for leaching event five to

eight. This trend was the same for Zn where concentrations in the leachate of the control were higher than biochar treatments for leaching events five and six, showing that sewage sludge biochar retained the Cu and Zn. This retention was explained by the sorption behaviour shown in the sorption experiment that used the same effluent (Chapter 5). The high ash and P contents and pH of the sewage sludge biochar, in addition to the neutral pH of the soil, facilitated precipitation of the metals and reduced their mobility. This view was supported by the fact that 95% (5% in leachate) of recovered Zn was in the control soil while 97% (3% in leachate) was for the soil amended with biochar at 100 t ha⁻¹. The low Cu and Zn in the leachate suggest that sorption of these metals on sewage sludge biochar has potential to limit leaching of these elements to groundwater. The effects of this immobilization of Cu and Zn in soil amended with sewage sludge on dry matter of spinach irrigated with dilute effluent were not clear.

Increasing rates of latrine waste and sewage sludge biochar pyrolysed at 350°C showed insignificant effect on dry-matter of spinach irrigated with industrial effluent. This suggested that the agronomic properties of biochar were masked by the neutral pH of the soil and the acidic nature of the effluent and heavy metal concentration. The relatively high EC values of industrial effluent compared to tap water could explain the lower plant water, possibly as affected by osmotic potential, hindering water uptake. In addition to the toxic effects of Cu in the roots, limited water uptake could explain the lower shoot and root dry-matter. The extractable Zn levels were high as a result of effluent rich in Zn. The higher root tissue Cu than Zn, where effluent was used, indicates that more Cu was mobile in the soil because reduced sorption by competition with Zn. This is supported by the lower sorption of Cu and higher sorption of Zn from multiple metal effluent, on latrine waste and sewage sludge biochar (Chapter 5). The high tissue Cu and undetectable extractable Cu in soil after spinach cultivation, show that biochar application increases the mobility and uptake of Cu, while the rest is retained in unavailable form, measured as total Cu. Industrial effluent is capable of inducing and aggravating heavy metal concentration in plant tissue, especially Cu following biochar application.

This study showed that spinach biomass was higher for sewage sludge biochar than latrine waste biochar when tap water was used. Sewage sludge biochar can be regarded as an amendment that supplies micronutrients. Glaser et al. (2002) reported that biochar may be added to the soil as a source of plant nutrients and nutrient retention conditioner. Low pyrolysis temperature biochar is reported to have the potential to release plant nutrients as they degrade (Trupiano et al., 2017; Aly, 2016).

8.2 Conclusion

Latrine waste and sewage sludge biochars have higher pH, ash and total P contents than pine-bark. Sorption of Cd, Cu and Zn are higher on latrine waste and sewage sludge biochar than pine-bark biochar. Latrine waste biochar has higher ash and Cd sorption capacity than sewage sludge biochar. In mixtures, pine-bark biochar and latrine waste or sewage sludge biochar have synergistic effects on the sorption of Cd. While latrine waste biochar was more effective for removal of Cu, Zn and Cr from the single-metal, sewage sludge biochar was more effective for multiple metal effluents. Even though in the controlled batch equilibrium studies, the faecal waste biochar appeared to enhance immobilization of heavy metals, in column study and pot trial, they did not significantly enhance metal immobilization and appeared to enhance certain plant uptake of the metals from effluent. Amendment of a neutral loam soil with 50 and 100 t ha⁻¹ sewage sludge biochar did not significantly enhance Cu and Zn immobilization or limit leaching from the soil when treated with industrial effluent. Application of faecal waste biochar at 50 and 100 t ha⁻¹ significantly enhanced mobility of Cu in the soil and tissue concentration of spinach irrigated with dilute industrial effluent. Competitive sorption between Zn and Cu from an effluent with high Zn concentrations, on biochar-amended soil, results in greater mobility of Cu in soil and increase its uptake by plants. Only sewage sludge biochar produced at 350°C can be regarded as a source of micronutrients, Cu and Zn, for spinach when applied at 50 and 100 t ha⁻¹ and irrigated with tap water.

8.3 Recommendations

- (a) Given the ambivalent face of biochar attributed to contaminant release, it is recommended that the selection of feedstock and pyrolysis conditions for production of intended biochar for given use be succinctly conducted.
- (b) The findings from this study suggest necessary funding to support implementation of parallel and or similar studies replicated in more areas, more soil types, and more crops and preferably under field conditions. A database on characteristics and application of biochar from locally available feedstocks can be initiated, with the view of harmonizing legislation related biochar production and use.
- (c) Further studies need to focus on the using biochar from sewage sludge and latrine waste to sorb heavy metals from industrial effluents, at larger practical application scale.
- (d) Alternate use of effluent and freshwater could be tested to explore its impact on sorption of metals and beneficial effects of biochar on biomass production of given crops.

REFERENCES:

- Abild-Pedersen, F., Greeley, J., Studt, F., Rossmeisl, J., Munter, T. R., Moses, P. G., Skulason, E., Bligaard, T., and Nørskov, J. K. 2007. Scaling properties of adsorption energies for hydrogen-containing molecules on transition-metal surfaces. *Physical Review Letters*, 99 1, 4 – 7. <https://doi.org/10.1103/PhysRevLett.99.016105>
- Abujabhah, I. S., Bound, S. A., Doyle, R., and Bowman, J. P., 2016. Effects of biochar and compost amendments on soil physicochemical properties and the total community within a temperate agricultural soil. *Applied Soil Ecology* 98, 243 – 253. <https://doi.org/10.1016/j.apsoil.2015.10.021>
- Agrafioti, E., Bouras, G., Kalderis, D., and Diamadopoulos, E., 2013. Biochar production by sewage sludge pyrolysis. *Journal of Analytical and Applied Pyrolysis* 101, 72 – 78. <https://doi.org/10.1016/j.jaap.2013.02.010>
- Ahluwalia, S.S. and Goyal, D., 2007. Microbial and plant derived biomass for removal of heavy metals from wastewater. *Bioresource Technology* .98, 2243 – 2257.
- Ahmad, M., Lee, S. S., Dou, X., Mohan, D., Sung, J. K., Yang, J. E., and Ok, Y. S. 2012. Effects of pyrolysis temperature on soybean stover- and peanut shell-derived biochar properties and TCE adsorption in water. *Bioresource Technology* 118, 536 – 544. <https://doi.org/10.1016/j.biortech.2012.05.042>
- Ahmad, M., Rajapaksha, A. U., Lim, J. E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S. S., and Ok, Y. S., 2013. Biochar as a sorbent for contaminant management in soil and water: A review. *Chemosphere* Article in Press
- Ahmed, N., Rahman, M., Won, S., and Shim, S. 2017. Biochar properties and eco-friendly applications for climate change mitigation, waste management, and wastewater treatment: A review. *Renewable and Sustainable Energy Reviews*, 79 February, 255–273. <https://doi.org/10.1016/j.rser.2017.05.057>
- Alam, T., Arif, A., and Ahmad, E. 2017. Egyptian Journal of Basic and Applied Sciences Uptake of Cu 2 + and Zn 2 + from simulated wastewater using muskmelon peel biochar: Isotherm and kinetic studies. *Egyptian Journal of*

- Basic and Applied Sciences, 43, 236–248.
<https://doi.org/10.1016/j.ejbas.2017.06.006>
- Al-Hamaiedeh, H., and Bino, M., 2010. Effect of treated greywater reuse in irrigation on soil and plants. *Desalination* 256 2010 115 – 119.
- Ali, I., 2010. The quest for active carbon adsorbent substitutes: inexpensive adsorbents for toxic metal ions removal from wastewater. *Separation and Purification Reviews*. 39, 95 – 171
- Al-Khatib, A. I., Monou, M., Abu Zahra, A. S. F., Shaheen, H. Q., and Kassinos, D., 2010. Solid waste characterization, quantification and management practices in developing countries. A case study: Nablus district – Palestine. *Journal of Environmental Management* 91, 1131 – 1138.
- Alloway, B. J., 1995. “Soil processes and behaviour of metals”. *Heavy metals in soil*. 38 – 57.
- Al-wabel, M. I., Usman, A. R. A., El-naggar, A. H., Aly, A. A., Ibrahim, H. M., Elmaghraby, S., and Al-omran, A. 2015. Conocarpus biochar as a soil amendment for reducing heavy metal availability and uptake by maize plants. *Saudi Journal of Biological Sciences*, 224, 503–511.
<https://doi.org/10.1016/j.sjbs.2014.12.003>
- Aly, H. M. 2016. Biochar and its importance in adsorption of antibiotic and heavy metals from aqueous solutions, 1993, 75–78. SHORT COMMUNICATION
- Amonette. J. E., and Joseph, S., 2009. Characteristics of biochar: microchemical properties.
- Aspe, E., and Fernandez, K., 2011. Comparison of phenolic extracts obtained of *Pinus radiata* bark from pulp and paper industry and sawmill industry. *Maderas. Ciencia Tecnologia*. 13 3: 243 – 252, 2011.
- Austin, A., 2002. Health aspects of ecological sanitation. *EcoSanRes* 2002
- Austin, L. M., 2006. Operation safety of urine diversion toilets in Durban, South Africa. 32nd WEDC International Conference, Colombo, Sri Lanka, 2006.
- Aziz, H. A., Adlan, M. N., and Ariffir, K. S., 2008. Heavy metals Cd, Pb, Zn, Ni, Cu and Cr III removal from water in Malaysia: Post-treatment by high-quality limestone. *Bioresource Technology* 99, 1578–1583

- Bame, I. B., Hughes, J. C., Titshall, L.W., and Buckley, C. A., 2013. Leachate characteristics as influenced by application of anaerobic baffled reactor effluent to three soils: A soil column study. *Chemosphere* 93, 2171 – 2179.
- Bamminger, C., Marschner, B., and Juschke, E., 2014. An incubation study on the stability and biological effects and pyrogenic and hydrothermal biochar in two soils. *European Journal of Soil Science* 2014 65: 72 – 82.
- Baronti, S., Vaccari, F. P., Miglietta, F., Calzolari, C., Lugato, E., Orlandini, S., Pini, R., Zulian, C., and Genesio, L., 2014. Impact of biochar application on plant water relations in *Vitis vinifera* L. *European Journal of Agronomy* 53, 38 – 44.
- Batool, S. A., and Ch, M. N., 2009. Municipal solid waste management in Lahore City District, Pakistan. *Waste Management* 29: 1971–1981.
- Beesley, L. and Marmiroli, M., 2011. The immobilisation and retention of soluble arsenic, cadmium and zinc by biochar. *Environmental Pollution* 159, 474 - 480.
- Bell, M. J., and Worrall, F., 2011. Charcoal addition to soils in NE England: a carbon sink with environmental co-benefits? *Science of the Total Environment* 409, 1704 – 1714.
- Benjamin, M. M., and Leckie, J. O. 1981. Competitive adsorption of cd, cu, zn, and pb on amorphous iron oxyhydroxide. *Journal of Colloid And Interface Science*, 832, 410–419. [https://doi.org/10.1016/0021-9797\(81\)90337-4](https://doi.org/10.1016/0021-9797(81)90337-4)
- Berthouex, P. M., and Brown, L. C., 2013. Pollution prevention and control. Paul Mac Berthouex & Linfield C Brown & bookboon.com ISBN: 978-87-403-0526-5.
- Biernacka, E., and Małuszyński, M. J. 2006. The Content of Cadmium, Lead and Selenium in Soils from Selected Sites in Poland. *Polish J. Environ. Stud.* Vol. 15, No. 2a, 7-9
- Black, Scott. 1986. “Microenvironment Soil pH around Broadcast Urea Granules and Its Relationship to Ammonia Volatilization.” July
- Bogusz, A., Oleszczuk, P., and Dobrowolski, R., 2015. Application of laboratory prepared and commercially available biochars to adsorption of cadmium, copper and zinc ions from water. *Bioresource Technology* 196, 540 – 549.

- Brewer, C. E., Unger, R., Schmidt-Rohr, K., & Brown, R. C. 2011. Criteria to Select Biochars for Field Studies based on Biochar Chemical Properties. *Bioenergy Research*. 4, 312 – 323. <https://doi.org/10.1007/s12155-011-9133-7>
- Buamscha, M. G., Altland, J. E., Sullivan, D. M., Horneck, D. A., and Cassidy, J., 2007. Chemical and physical properties of Douglas fir bark relevant to the production of container plants. *Hort. Science* 42 5: 1281 – 1286.
- Buss, W., Graham, M. C., Shepherd, J. G., & Mašek, O., 2016. Suitability of marginal biomass-derived biochars for soil amendment. *Science of the Total Environment*. 547, 314 – 322 <https://doi.org/10.1016/j.scitotenv.2015.11.148>
- Cantrell, K. B., Hunt, P. G., Uchimiya, M., Novak, J. M., and Ro, K. S. 2012. Impact of pyrolysis temperature and manure source on physicochemical characteristics of biochar. *Bioresource Technology*. <https://doi.org/10.1016/j.biortech.2011.11.084>
- Cao, X. 2017. RSC Advances Application of biochar-based catalysts in biomass upgrading : a review. *RSC Advances*, 7, 48793–48805. <https://doi.org/10.1039/C7RA09307A>
- Chan, K. Y., Van Zwieten, L., Meszaros, I., Downie, A., and Joseph, S., 2007. Agronomic values of green waste biochar as a soil amendment. *Australian Journal of Soil Research* 45: 629 – 634.
- Chen, M., and Ma, L. Q., 2001. Comparison of three aqua regia digestion methods for twenty Florida soils. *Soil Sci, Soc. Am, J.* 65: 491 – 499.
- Chen, X., Chen, G., Chen, L., Chen, Y., Lehmann, J., McBride, M. B., & Hay, A. G. 2011. Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution. *Bioresource Technology*. <https://doi.org/10.1016/j.biortech.2011.06.078>
- Chen, Y., Shinogi, Y., and Taira, M., 2010. Influence of biochar use on sugarcane growth, soil parameters and groundwater quality. *Australian Journal of Soil Research* 48: 526 – 530.
- Cheng, C. H., and Lehmann, J., 2009. Ageing of black carbon along a temperature gradient. *Chemosphere* 75 8, 1021 – 1027.

- Cheng, C. H., Lehmann, J., Thies, J. E., and Burton, S. D., 2008. Stability of black carbon in soils across a climatic gradient. *J. Geophys. Res.* 113, 1-10.
- Cheremisinoff, N. P., 2003. *Handbook of solid waste management and waste minimization technologies*. Butterworth – Heinemann. ISBN 0080507816, 9780080507811
- Chowdhury, S. R., and Yanful, E. K., 2010. Arsenic and chromium removal by mixed magnetite -maghemite nanoparticle and the effect of phosphate on removal. *Journal of Environmental Management* 91, 2238e2247
- Chun Y., Sheng G., Y., and Chou, C. T., 2004. Compositions and sorptive properties of crop residue-derived chars. *Environ Sci. Technol.* 38, 4649 – 4655.
- Clemente, R., and Bernal, M. P. 2006. Fractionation of heavy metals and distribution of organic carbon in two contaminated soils amended with humic acids. *Chemosphere*, 64, 1264– 1273.
- Coates, J., 2000. Interpretation of Infrared Spectra, a Practical Approach. In: Meyers, R.A. Ed., *Encyclopedia of Analytical Chemistry*. John Wiley & Sons Ltd, Chichester, pp. 10815 – 10837.
- Coumar, M. V., Parihar, R. S., Dwivedi, A. K., Saha, J. K., Rajendiran, S., Dotaniya, M. L., and Kundu, S., 2016. Impact of pigeon pea biochar on cadmium mobility in soil and transfer rate to leafy vegetable spinach. *Environmental Monitoring and Assessment* 2016 188:31 <https://doi.org/10.1007/s10661-015-5028-y>
- Cui, L., Yan, J., Li, L., Quan, G., Ding, C., Chen, T., Yin, C., Gao, J., and Hussain, Q. 2015. Does biochar alter the speciation of Cd and Pb in aqueous solution? *BioResources* 10 (1) 88 – 104.
- Dai, Z., Meng, J., Shi, Q., Xu, B., Lian Z., Brookes, P. C., and Xu, J.-M., 2016. Effects of manure and lignocelluloses-derived biochars on adsorption and desorption of zinc by acidic types of soil with different properties. *European Journal of Soil Science*, January, 67, 40 – 50.
- Das, P., Samantaray, S., and Rout, G. R., 1997. Studies on cadmium toxicity in plants: A review. *Environmental Pollution* 98 (1) 29 – 36.
- Derakhshan, Z., Myung, N., and Jung, C., 2017. “The Effects of Biochar and Inorganic Amendments on Soil Remediation in the Presence of Hyperaccumulator

- Plant.” *International Journal of Energy and Environmental Engineering* 84:317–29.
- Desta, M. B., 2013. Batch sorption experiments: Langmuir and Freundlich isotherm studies for the adsorption of textile metal ions onto Teff straw *Eragrostis tef* agricultural waste. Hindawi Publishing Corporation, *Journal of Thermodynamics* 2013, Article ID 375830, 6 pages.
- di Toppi, L. S., and Gabbrielli, R., 1999. Response to cadmium in higher plants. *Environmental and Experimental Botany* 41, 105 – 130.
- Diawara, M. M., Litt, J. S., Unis, D., Alfonso, N., Martinez, LA., Crock, J. G., Smith, D. B., and Casrsella, J., 2006. Arsenic, Cadmium, Lead, and Mercury in surface soils, Pueblo, Colorado: implications for population health risk. *Environmental Geochemistry and Health*, 28: 297 – 315.
- Ding, W., Dong, X., Ime, I.M., Gao, B., and Ma, L.Q., 2014. Pyrolytic temperatures impact lead sorption mechanisms by bagasse biochars. *Chemosphere* 105, 68–74.
- Do Thuy, T., Molbak, K., PhungDac, C., and Dalsgaard, A., 2007. Helminth infections among people using wastewater and human excreta in peri-urban agriculture and aquaculture in Hanoi, Vietnam. *Tropical Medicine and International Health* 12 Suppl. 2, 82 – 90.
- Doble, M., and Kumar, A. 2005. *Biotreatment of industrial effluents*. Elsevier Butterworth–Heinemann: UK ISBN: 0-7506-7838-0.
- Downie, A. E., Van Zwieten, L., Smernik, R. J., Morris, S., and Munroe, P. R., 2011. Terra preta Australis: reassessing the carbon storage capacity of temperate soils. *Agriculture, Ecosystems and Environment* 140, 137 – 147.
- Dumroese, R. K., Heiskanen, J., Englund, K., and Tervahauta, A., 2011. Pelleted biochar: chemical and physical properties show potential use as a substrate in container nurseries. *Biomass and Bioenergy* 35, 2018 – 2027.
- Duruibe, J. O., Ogwuegbu, C. and Egwurugwu, J. N., 2007. Heavy metal pollution and human biotoxic effects. *International Journal of Physical Sciences*, 2 5 112–118. <http://www.academicjournals.org/IJPS>

- Eazhilkrishna, N., Thilagavathi, T., and Baskar, M. 2017. Effect of Nutrient Enriched Biochar on Yield and NPK Uptake of Maize Grown in Alfisol, 67, 1326–1334.
- Enders, A., Hanley, K., Whitman, T., Joseph, S., and Lehmann, J., 2012. Characterization of biochars to evaluate recalcitrance and agronomic performance. *Bioresource Technology*, 114: 644 – 653.
- Erlandsson, M., and Sundquist, J., 2014. Environmental consequences of different recycling alternatives for wood waste. Swedish Environmental Research Institute. IVL Report B 2182.
- Fellet, G., Marchiol, L., Vedove, G. D., and Peressotti, A., 2011. Application of biochar on mine tailings: effects and perspectives for land reclamation. *Chemosphere* 83, 1262 – 1267. <https://doi.org/10.1016/j.chemosphere.2011.03.053>
- Fidjeland, J., Magri, M. E., Jonsson, H., Albiñ, A., and Vinneras, B., 2013. The potential for self-sanitization of the fecal sludge by intrinsic ammonia. *Water Research* 47 2013 6014 – 6023.
- Food and Agriculture Organization of the United Nations FAO 2015. FAO Forestry Series No. 48 FAO Statistics Series No. 204, Forest Products 2009-2013. Rome, Italy. <http://www.fao.org/3/a-i4746m.pdf>
- Forján, R., Asensio, V., Rodríguez-Vila, A., & Covelo, E. F., 2016. Contribution of waste and biochar amendment to the sorption of metals in a copper mine tailing. *Catena*. 137 2016 120 – 125 <https://doi.org/10.1016/j.catena.2015.09.010>
- Gao, Y., Zhu, B., He, N., Yu, G., Wang, T., Chen, W., and Tian, J., 2014. Phosphorus and carbon competitive sorption-desorption and associated non-point loss respond to natural rainfall events. *Journal of Hydrology* 517, 447 – 457.
- Gasco, G., Paz-Ferreiro, J., and Mendez, A., 2012. Thermal analysis of soil amended with sewage sludge and biochar from sewage sludge pyrolysis. *J Therm Anal Calorim*, 108: 769 – 775.
- German Technical Cooperation GTZ, 2010. Basic overview of composting toilets with or without urine diversion. Technology review “composting toilets”. <http://www.gtz.de/en/themen/umweltinfrastruktur/wasser/9397.htm>

- Ghosh, M., and Singh, S. P., 2005. A comparative study of cadmium phytoextraction by accumulator and weed species. *Environ. Pollut.* 133: 365–371.
- Glaser, B., Lehmann, J., and Zech, W. 2002. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal - A review. *Biology and Fertility of Soils*. 35: 219 – 230. <https://doi.org/10.1007/s00374-002-0466-4>
- Glaser, B., Lehmann, J., Steiner, C., Nehls, T., Yousaf, M., and Zech, W., 2002. Potential of pyrolyzed organic matter in soil amelioration. In 12 ISCO conference, Beijing, 421 – 427.
- Gomez, J. D., Denef, K., Stewart, C. E., Zheng, J., and Cotrufo, M. F., 2014. Biochar addition rate influences soil microbial abundance and activity in temperate soils. *European Journal of Soil Science*, January, 65, 28 – 39.
- González-Viar, M., Díez-Montero, R., Molinos-Senante, M., De-Florio, L., Esteban-García, A. L., Sala-Garrido, R., Hernández-Sancho, F., and Tejero, I., 2016 Cost-effectiveness analysis of sewer mining versus centralized wastewater treatment: Case study of the Arga river basin, Spain, *Urban Water Journal*, 13:3, 321-330, DOI: 10.1080/1573062X.2014.991742
- Gray, C. W., McLaren, R. G., Roberts, A. H. C., & Condrón, L. M., 1999. Solubility, sorption and desorption of native and added cadmium in relation to properties of soils in New Zealand. *European Journal of Soil Science*. 50, 127 - 137 <https://doi.org/10.1046/j.1365-2389.1999.00221.x>
- Han, F. X., Banin, A., Su, Y., Monts, D. L., Plodinec, M. J., Kingery, W. L., and Triplett, G. E., 2002. Industrial age anthropogenic inputs of heavy metals into the pedosphere. *Naturwissenschaften*, 89: 497 – 504
- Hegazi, H. A. 2013. Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents. *HBRC Journal*, 9 3, 276 – 282. <https://doi.org/10.1016/j.hbrcj.2013.08.004>
- Heinonen-Tanski, H., and van Wijk-Sijbesma, C., 2005. Human excreta for plant production. *Bioresource Technol.* 96 4, 403 – 411.

- Herath, H. M. S. K., Camps-Arbestain, M., and Hedley, M., 2013. Effect of biochar on soil physical properties in two contrasting soils: An Alfisol and an Andisol. *Geoderma* 209 – 210, 188 – 197.
- Hmid, A., Mondelli, D., Fiore, S., Fanizzi, F. P., Chami, Z. A., and Dumontet, S., 2014. Production and characterization of biochars from three-phase olive mill waste through slow pyrolysis. *Biomass and Bioenerg.* 71, 330-339.
- Hossain, M. K., Strezov, V., Yin Chan, K., Ziolkowski, A., and Nelson, P. F., 2011. Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar. *Journal of Environmental Management* 92, 223 – 228.
- Huang, Y., Anderson, M., McIlveen-Wright, D., Lyons, G. A., McRoberts, W. C., Wang, Y. D., Roskilly, A. P., and Hewitt, N. J., 2015. Biochar and renewable energy generation from poultry litter waste: A technical and economic analysis based on computational simulations. *Applied Energy* 160, 656 – 663.
- Hussain, A., Maitra, J., & Ali, K. 2017. Development of biochar and chitosan blend for heavy metals uptake from synthetic and industrial wastewater. *Applied Water Science*. <https://doi.org/10.1007/s13201-017-0604-7>
- Hwang, I. H., Ouchi, Y., and Matsuto, T., 2007. Characteristics of leachate from pyrolysis residue of sewage sludge. *Chemosphere* 68, 1913 – 1919.
- Inyang, M., Gao, B., Ding, W., Pullammanappallil, P., Zimmerman, A. R., and Cao, X., 2011. Enhanced lead sorption by biochar derived from anaerobically digested sugarcane bagasse. *Sep. Sci. Technol.* 46 12 1950 – 1956. <https://doi.org/10.1080/01496395.2011.584604>
- Inyang, M., Gao, B., Yao, Y., Xue, Y., Zimmerman, A. R., Pullammanappallil, P., and Cao, X., 2012. Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass. *Bioresource Technology* 110, 50 – 56.
- Ireland, R. C., 2010. *Experimental Statistics for Agriculture and Horticulture*. United Kingdom: Cambridge University Press. ISBN 978-1-84593-537-5.
- Jeffery, S., Verheijen, F. G. A., van der Velde, M., and Bastos, A. C., 2011. A quantitative review of the effects of biochar application on soils on crop

- productivity using meta-analysis. *Agriculture, Ecosystems and Environment* 144, 175 – 187. <https://doi.org/10.1016/j.agee.2011.08.015>
- Jien, S.-H., and Wang, C.-S., 2013. Effects of biochar on soil properties and erosion potential in a highly weathered soil. *Catena* 110, 225 – 233.
- Jimenez, B., Austin, A., Cloete, E., and Phasha, C., 2006. Using Ecosan sludge for crop production. *Water Science & Technology*, 54 5: 169 – 177.
- Jimenez, B., Drechsel, P., Kone, D., Bahri, A., Raschid-Sally, L., and Qadir, M., [2009]. Wastewater, sludge and excreta use in developing countries: an overview.
- Jin, H., Hanif, M. U., Capareda, S., Chang, Z., Huang, H., and Ai, Y., 2016. CopperII removal potential from aqueous solution by pyrolysis biochar derived from anaerobically digested algae-dairy-manure and effect of KOH activation. *Journal of Environmental Chemical Engineering* 4, 365 – 372.
- Joseph, S. D., Camps-Arberstain, M., Lin, Y., Munroe, P., Chia, C. H., Hook, J., van Zwieten, L., Kimber, S., Cowie, A., Singh, B. P., Lehmann, J., Foidl, N., Smernik, R. J., and Amonette, J. E., 2010. An investigation into the reactions of biochar in soil. *Australian Journal of Soil Research*, 48, 501 – 515.
- Kabata-Pendias, A., 2000. Trace elements in soils and plants. CRC Press: London.
- Kadirvelu, K., Thamaraiselvi, K., and Namasivayam, C. 2001. Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. *Bioresource Technology*, 761, 63–65. <https://doi.org/10.1016/S0960-85240000072-9>
- Kammann, C. I., Linsel, S., Gobling, J. W., and Koyro, H.-W., 2011. Influence of biochar on drought tolerance of *Chenopodium quinoa* wild and on soil-plant relations. *Plant Soil* DOI 10.1007/s11104-011-0771-5
- Karhu, K., Mattila, T., Bergstorm, I., and Regina, K., 2011. Biochar addition to agricultural soil increased CH₄ uptake and water holding capacity – results from a short-term pilot field study. *Agriculture, Ecosystems and Environment* 140, 309 – 313. <https://doi.org/10.1016/j.agee.2010.12.005>

- Keiluweit, M., Nico, P.S., Johnson, M.G., Kleber, M., 2010. Dynamic molecular structure of plant biomass-derived black carbon biochar. *Environ. Sci. Technol.* 44, 1247–1253.
- Khan, S., Waqas, M., Ding, F., Shamshad, I., Arp, H. P. H., and Li, G., 2015. The influence of various biochars on the bioaccessibility and bioaccumulation of PAHs and potentially toxic elements to turnips *Brassica rapa* L.. *Journal of Hazardous Materials* 300, 243 – 253.
- Khodaverdiloo, H., and Samadi, A. 2011. Batch equilibrium study on sorption, desorption, and immobilisation of cadmium in some semi-arid zone soils as affected by soil properties. *Soil Research*, 495. <https://doi.org/10.1071/SR10156>
- Kim, K. H., Kim, J.-Y., Cho, T.-S., and Choi, J. W., 2012. Influence of pyrolysis temperature on physicochemical properties of biochar obtained from the fast pyrolysis of pitch pine *Pinus rigida*. *Bioresource Technology* 118, 158 – 162.
- Kim, W.-K., Shim, T., Kim, Y.-S., Hyun, S., Ryu, C., Park, Y.-K., and Jung, J., 2013. Characterization of cadmium removal from aqueous solution by biochar produced from a giant *Miscanthus* at different pyrolytic temperatures. *Bioresour. Technol.* 138, 266 – 270.
- Kirkeby, J. T., Birgisdottir, H., Bhandar, G. S., Hauschild, M., and Christensen, T. H., 2007. Modelling of environmental impacts of solid waste landfilling within the life-cycle analysis program EASEWASTE. Elsevier Ltd. doi: 10.1016 /j. wasman. 2006. 06.017. Available online 26 March 2007
- Kiziloglu, F. M., Turan, M., Sahin, U., Kuslu, Y., and Dursun, A. 2008. Effects of untreated and treated wastewater irrigation on some chemical properties of cauliflower *Brassica oleracea* L. var. botrytis and red cabbage *Brassica oleracea* L. var. rubra grown on calcareous soil in Turkey. *Agricultural Water Management*, 95 6, 716 – 724. <https://doi.org/10.1016/j.agwat.2008.01.008>
- Kloss, S., Zehetner, F., Dellantonio, A., Hamid, R., Ottner, F., Liedtke, V., Schwanninger, M., Gerzabek, M. H., and Soja, G., 2012. Characterization of slow pyrolysis biochars: effects of feedstocks and pyrolysis temperature on biochar properties. *J. Environ. Qual.* 41, 990 – 1000.

- Knowles, O. A., Robinson, B. H., Contangero, A., and Clucas, L., 2011. Biochar for the mitigation of nitrate leaching from soil amended with biosolids. *Science of the Total Environment* 409, 3206 – 3210.
- Koetlisi A Koetlisi and Pardon Muchaonyerwa. 2018 Pyrolysis Temperature Effects on Yield, Physico-chemical Characteristics of Pine-bark Biochars and Cadmium Sorption. *Indian Journal of Environmental Protection*, 38 3: 197 – 212 2018
- Koetlisi, K. A., and Muchaonyerwa, P. 2017. Biochar Types from Latrine Waste and Sewage Sludge Differ in Physico-Chemical Properties and Cadmium Adsorption. *American Journal of Applied Sciences*, 14 11, 1039 – 1048. <https://doi.org/10.3844/ajassp.2017.1039.1048>
- Kolodynska, D., Wnetrzak, R., Leahy, J. J., Hayes, M. H. B., Kwapinski, W., and Hubicki, Z., 2012. Kinetic and adsorptive characterization of biochar in metal ions removal. *Chemical Engineering Journal* 197, 295 – 305.
- Kumar, S., Loganathan, V. A., Ram B. Gupta, R. B., and Barnett, M. O., 2011. An Assessment of UVI removal from groundwater using biochar produced from hydrothermal carbonization. *Journal of Environmental Management* 92, 2504 – 2512.
- Kuppusamy, S., Thavamani, P., Megharaj, M., Venkateswarlu, K., and Naidu, R. 2016. Agronomic and remedial benefits and risks of applying biochar to soil: Current knowledge and future research directions. *Environment International* 87, 1 – 12. <https://doi.org/10.1016/j.envint.2015.10.018>
- Kutu, F.R., Muchaonyerwa, P. and Mnkeni, P.N.S., 2010. Complementary nutrient effects of separately collected human faeces and urine on the yield and nutrient uptake of spinach *Spinaciaoleracea*. *Waste Manage. Res.* 29 5, 532 – 539.
- Laird, David A. 2008. “The Charcoal Vision: A Win-Win-Win Scenario for Simultaneously Producing Bioenergy, Permanently Sequestering Carbon, While Improving Soil and Water Quality.” *Agronomy Journal* 1001:178–81.
- Larney, F. J., and Angers, D. A., 2012. The role of organic amendments in soil reclamation: A review. *Canadian Journal of Soil Science*, 92: 19 – 38.

- Larsbo, M., Löfstrand, E., van Alphen de Veer, D., and Ulén, B., 2013. Pesticide leaching from two Swedish topsoils of contrasting texture amended with biochar. *Journal of Contaminant Hydrology* 147 2013 73 – 81.
- Lee, J.W., Kidder, M., Evans, B.R., Paik, S., Buchanan III, A.C., Garten, C.T., Brown, R.C., 2010. Characterization of biochars produced from corn stovers for soil amendment. *Environ. Sci. Technol.* 44, 7970–7974.
- Lehmann, J. and Joseph, S., 2009. Biochar for environmental management: science and technology. Earthscan: London pp 33 – 43.
- Lehmann, J., da Silva Jr., J. P., Steiner, C., Nehls, T., Zech W., and Glaser, B., 2003. Nutrient availability and leaching in an archaeological Anthrosol and a Ferralsol of the Central Amazon basin: fertilizer, manure and charcoal amendments. *Plant and Soil*, 249: 343 – 357.
- Li, H., Ye, X., Geng, Z., Zhou, H., Guo, X., Zhang, Y., Wang, G., 2016. The influence of biochar type on long-term stabilization for Cd and Cu in contaminated paddy soils. *Journal of Hazardous Materials*. 304, 40 – 48 <https://doi.org/10.1016/j.jhazmat.2015.10.048>
- Li, J., Li, Y., Wu, Y., and Zheng, M., 2014. A comparison of biochars from lignin, cellulose and wood as the sorbent to an aromatic pollutant. *Journal of Hazardous Materials* 280, 450 – 457.
- Liang, C., Xiao-Hua, L., Zhen-Hua, Z., Xiao-Tao, Z., Rengel, Z., and Zhao-Pu, L., 2011. Cadmium Accumulation and Translocation in Two Jerusalem Artichoke *Helianthus tuberosus* L. Cultivars. *Pedosphere*, 215: 573 – 580.
- Lin, Y., Munroe, P., Joseph, S., Ziolkowski, A., van Zwieten, L., Kimber, S., and Rust, J., 2013. Chemical and structural analysis of enhanced biochars: thermally treated mixtures of biochar, chicken litter, clay and minerals. *Chemosphere* 91 2013 35 – 40.
- Linder, S., and Lundehn, C., 2002. Metals in sewage sludge in the Eastern Cape. Sweden: Chalmers University of Technology.
- Liu, N., Charrua, A. B., Weng, C.-H., Yuan, X., and Ding, F., 2015. Characterization of biochars derived from agriculture wastes and their adsorptive removal of

- atrazine from aqueous solution: A comparative study. *Bioresource Technology* 198 2015 55 – 62.
- Liu, X., Li, Z., Zhang, Y., Feng, R., and Mahmood, I. B. 2014. Characterization of human manure-derived biochar and energy-balance analysis of slow pyrolysis process. *Waste Management*. 34, 1619 – 1626. <https://doi.org/10.1016/j.wasman.2014.05.027>
- Luo, Y., Durenkamp, M., Nobili, M. D., Lin, Q., and Brookes P. C., 2011. Short-term soil priming effects and the mineralization of biochar following its incorporation to soils of different pH. *Soil Biology and Biochemistry* 43 2011 2304 – 2314.
- Madungwe, E., and Sakuringwa, S., 2007. Greywater reuse: A strategy for water demand management in Harare? *Physics and Chemistry of the Earth* 32, 1231 – 1236.
- Major, J., 2011. Biochar for soil remediation and land reclamation. *International Biochar Initiative Research Summaries*. info@biochar-international.org
- Major, J., Rodon, M., Molina, D., Riha, S. J., and Lehmann, J., 2010. Maize yield and nutrition during four years after biochar application to a Colombian savannaoxisol. *Plant Soil*, 333: 117 – 128.
- Malik, R. N., Husain, S. Z., and Nazir, I. 2010. Heavy metal contamination and accumulation in soil and wild plant species from industrial area of Islamabad, Pakistan. *Pakistan Journal of Botany*, 42 1, 291 – 301.
- Manai, I., Miladi, B., El Mselmi, A., Smaali, I., Hassen, A. B., Hamdi, M., and Bouallagui, H., 2016. Industrial textile effluent decolourization in stirred and static batch cultures of a new fungal strain *Chaetomium globosum* IMA1 KJ472923. *Journal of Environmental Management* 170, 8 – 14.
- Manfredi, S., and Christensen, T. H., 2009. Environmental assessment of solid waste landfilling technologies by means of LCA-modelling. *Waste Management* 29 2009 32 – 43.
- Maraseni, T. N. 2010. Biochar: maximising the benefits. *International Journal of Environmental Studies*, 673, 319–327. <https://doi.org/10.1080/00207231003612225>

- Martinez, F., Cuevas, G., Iglesias, T., and Walter, I., 2002. Urban organic wastes effects on soil chemical properties in a degraded semi-arid ecosystem. Symposium 20, Paper 2103. 17th World Congress of Soil Science, 14 – 21 August 2002, Thailand.
- Massoud, M. A., Tarhini, A., and Nasr, J. A. 2009. Decentralized approaches to wastewater treatment and management: Applicability in developing countries. *Journal of Environmental Management*, 90 1, 652 – 659. <https://doi.org/10.1016/j.jenvman.2008.07.001>
- Masto, R. E., Ansari, M. A., George, J., Selvi, V. A., and Ram, L. C. 2013. Co-application of biochar and lignite fly ash on soil nutrients and biological parameters at different crop growth stages of *Zea mays*. *Ecological Engineering*, 58, 314–322. <https://doi.org/10.1016/j.ecoleng.2013.07.011>
- Mcbride, M. B., 1995. Toxic metal accumulation from agricultural use of sludge: Are USEPA regulations protective? *Journal of Environmental Quality*, 24 1: 5 – 18.
- McKay, G., and Porter, J. F., 1997. Equilibrium parameters for the sorption of copper, cadmium and zinc ions onto peat. *Journal of Chemical Technology and Biotechnology* 69 3, 309 - 320.
- Mead, D. J., 2013. Sustainable management of *Pinus radiata* plantations. FAO Forestry Paper No. 170. Rome, FAO.
- Mendez, A., Gomez, A., Paz-Ferreiro, J., and Gasco, G., 2012. Effects of sewage sludge biochar on plant metal availability after application to a Mediterranean soil. *Chemosphere* 89, 1354 – 1359.
- Merlic, C. A., 1997. WebSpetra: problems in NMR and IR spectroscopy. University of California. [n.p.]. Available from: < www.chem.ucla.edu/~webspectra/ > [Accessed: 01 October 2014].
- Metcalf, and Eddy, 2003. Wastewater engineering: treatment, disposal, and reuse, fourth ed. McGraw-Hill Publishing Company Ltd., New York.
- Mihelcic, J. R., Fry, L. M., and Shaw, R., 2011. Global potential of phosphorus recovery from human urine and feces. *Chemosphere* 84, 832 – 839.

- Miller, R. O., 1998. Microwave digestion of plant tissue in closed vessel. In: Kalra, Y. P., 1998. Handbook of reference methods for plant analysis. Taylor and Francis Group CRC Press; Washington DC.
- Mishra, S. R., Chandra, R., Kaila A., J., & Darshi B., S. 2017. Kinetics and isotherm studies for the adsorption of metal ions onto two soil types. *Environmental Technology & Innovation*, 7, 87–101. <https://doi.org/10.1016/j.eti.2016.12.006>
- Mitchell, P., Dalley, T. S. L., and Helleur, R. J., 2013. Preliminary laboratory production and characterization of biochars from lignocellulosic municipal waste. *Journal of Analytical and Applied Pyrolysis* 99, 71 – 78.
- Mnkeni, P. N. S., and Austin, L. M., 2009. Fertilizer value of human manure from pilot urine-diversion toilets. *Water SA*, 35 1: 133 – 138.
- Mohan, D., Kumar, H., Sarswat, A., Alexandre-Franco, M., Pittman Jr., C.U., 2014a. Cadmium and lead remediation using magnetic oak wood and oak bark fast pyrolysis bio-chars. *Chem. Eng. J.* 236, 513–528.
- Mohan, D., Pittman Jr., C. U., Bricka, M., Smith, F., Yancey, B., Mohammad, J., Steele, P. H., Alexandre-Franco, M. F., Gómez-Serrano, V., Gong, H., 2007. Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. *J. Colloid Interface Sci.* 310, 57 – 73.
- Mohan, D., Sarswat, A., Ok, Y.S., Pittman Jr., C.U., 2014b. Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent – a critical review. *Bioresour. Technol.* 160, 191–202. doi: <http://dx.doi.org/10.1016/j.biotech.2014.01.120>
- Montangero, A., Kone, D., and Strauss, M., 2002. Planning towards improved excreta management. Paper submitted to the IWA 5th Conference on Small Water and Wastewater Treatment Systems, Istanbul, Turkey, September 2002.
- Mosa, A., El-Banna, M. F., and Gao, B., 2016. Biochar filters reduced the toxic effects of nickel on tomato *Lycopersicon esculentum* L. grown in nutrient film technique hydroponic system. *Chemosphere* 149, 254 – 262.
- Moussa, M. D., Jill, S. L., Dave, U., Nicholas, A., Leeanne, M., James, G. C., David, B. S., & James, C. 2006. Arsenic, Cadmium, Lead, and Mercury in surface

- soils, Pueblo, Colorado: implications for population health risk. *Environmental Geochemistry and Health*, 28, 297–315.
- Muchuweti, M., Birkett, J.W., Chinyanga, E., Zvauya, R., Scrimshaw, M.D., and Lester, J.N., 2006. Heavy metal content of vegetables irrigated with mixtures of wastewater and sewage sludge in Zimbabwe: Implications for human health. *Agriculture, Ecosystems & Environment* 112, 41–48.
- Mukherjee, A., and Lal, R. 2014. The biochar dilemma. *Soil Research*, 52 3, 217. <https://doi.org/10.1071/SR13359>
- Mullen, C.A., Boateng, A.A., Goldberg, N.M., Lima, I.S., Laird, D.A., Hicks, K.B., 2010. Bio-oil and biochar production from corn cobs and stover by pyrolysis. *Biomass Bioenergy* 34, 67–74
- Nagajyoti, P.C., Lee, K.D. and Sreekanth, T.V.M. 2010 *Environ Chem Lett* 2010 8: 199. <https://doi.org/10.1007/s10311-010-0297-8>
- Namgay, T., Singh, B., & Singh, B. P. 2010. Influence of biochar application to soil on the availability of As, Cd, Cu, Pb, and Zn to maize *Zea mays* L. In *Australian Journal of Soil Research*, 48, 638 – 647. <https://doi.org/10.1071/SR10049>
- Nikiema, J., Cofie, O., Impraim, R., and Adamtey, N., 2013. Processing of fecal sludge to fertilizer pellets using a low-cost technology in Ghana. *Environment and Pollution*, Vol. 2 4 70 – 87.
- Novais, S.V., Zenero, M.D.O., Frade Junior, E.F., de Lima, R.P. and Cerri, C.E.P. 2017 Mitigation of Greenhouse Gas Emissions from Tropical Soils Amended with Poultry Manure and Sugar Cane Straw Biochars, 887 – 903. <https://doi.org/10.4236/as.2017.89065>
- Novak, J. M., Lima, I., Xing, B., Gaskin, J.W., Steiner, C., and Das, K.C., 2009. Characterization of designer biochar produced at different temperatures and their effects on a loamy sand. *Ann. Environ. Sci.* 3, 2.
- Ogbonnaya, U., and Semple, K. T., 2013. Impact of biochar on organic contaminants in soil. A tool for mitigating risk? *Agronomy*, 3 2: 349 – 375.
- Pandey, S. N., 2006. Accumulation of heavy metals Cd, Cr, Cu, Ni and Zn in *Raphanus sativus* L . and *Spinacia oleracea* L . plants irrigated with industrial

- effluent. *Journal of Environmental Biology* April 2006, 27 April, 381 – 384.
<https://doi.org/10.1016/j.apsusc.2013.07.033>
- Park, J. H., Ok, Y. S., Kim, S. H., Cho, J. S., Heo, J. S., Delaune, R. D., & Seo, D. C., 2016. Competitive adsorption of heavy metals onto sesame straw biochar in aqueous solutions. *Chemosphere*. 142, 77 – 83
<https://doi.org/10.1016/j.chemosphere.2015.05.093>
- Park, J., Cho, J., Ok, Y. S., Kim, S., Heo, J., Delaune, R. D., and Kim, S. 2016. Comparison of single and competitive metal adsorption by pepper stem biochar. *Archives of Agronomy and Soil Science*, 625, 617–632.
<https://doi.org/10.1080/03650340.2015.1074186>
- Pasztory, Z., Mohacsine, I. R., Gorbacheva, G., and Borcsok, Z., 2016. The utilization of tree bark. *BioResources* 11 3
- Pathak, A., Dastidar, M. G., and Sreekrishnan, T. R., 2009. Bioleaching of heavy metals from sewage sludge: a review. *Journal of Environmental Management* 90, 2343 – 2353.
- Paz-Ferreiro, J., Gasco, G., Gutierrez, B., and Mendez, A., 2012. Soil biochemical activities and the geometric mean of enzyme activities after application of sewage sludge and sewage sludge biochar to soil. *Biol. Fert. Soils* 48 5, 511 - 517. <http://dx.doi.org/10.1007/s00374-0110644-3>
- Peasy, A., 2000. Health aspects of dry sanitation with waste reuse. WELL studies in water and environmental health, task no. 324. London school of hygiene and tropical medicine.
- Pedrero, Francisco, Ioannis Kalavrouziotis, Juan José Alarcón, Prodromos Koukoulakis, and Takashi Asano. 2010. “Use of Treated Municipal Wastewater in Irrigated Agriculture-Review of Some Practices in Spain and Greece.” *Agricultural Water Management* 979:1233–41.
- Pellera, F.-M., and Gidarakos, E., 2015. Effect of dried olive pomace – derived biochar on the mobility of cadmium and nickel in soil. *Journal of Environmental Chemical Engineering* 3, 1163 – 1176.
- Peng, P., Lang, Y.-H., and Wang, X.-M., 2016. Adsorption behaviour and mechanism of pentachlorophenol on reed biochars: pH effect, pyrolysis temperature,

- hydrochloric acid treatment and isotherms. *Ecological Engineering* 90, 225 – 233.
- Pepper, I. L., Zerzghi, H., Brooks, J. P., and Gerba, C. P., 2008. Sustainability of land application of class B biosolids. *Journal of Environmental Quality* 2008 37: S58 – S67.
- Perez-Marin, A. B., Zapata, V. M., Ortuno, J. F., Aguilar, M., Saez, J., Llorens, M., 2007. Removal of cadmium from aqueous solutions by adsorption onto orange waste. *Journal of Hazardous Materials B139* 2007 122 – 131.
- Pinto, E., Sigaud-Kutner, T. C. S., Leitao, M. A. S., Okamoto, O. K., Morse, D., and Colepicolo, P. 2003. Heavy metal induced oxidative stress in algae. *J. Phycol.* 39, 1008 – 1018.
- Prasad, M. N. V., 1995. Cadmium toxicity and tolerance in vascular plants. *Environ. Exp. Bot.* 35: 525–545.
- Princeton University Library Data and Statistical Services., 2007. DSS – interpreting regression output. The trustees of Princeton University. Last updated March 2014. dss.princeton.edu/online_help/analysis/interpreting_regression.htm
- Puga, A. P., Melo, L. C. A., de Abreu, C. A., Coscione, A. R., and Paz-Ferreiro, J. 2016. Leaching and fractionation of heavy metals in mining soils amended with biochar. *Soil and Tillage Research*. <https://doi.org/10.1016/j.still.2016.01.008>
- Qadir, M., Wichelns, D., Raschid-Sally, L., McCornick, P. G., Drechsel, P., Bahri, A., and Minhas, P. S. 2010. “The Challenges of Wastewater Irrigation in Developing Countries.” *Agricultural Water Management* 974:561–68.
- Qdais, H. A., 2007. Environmental impact assessment of municipal solid waste landfills: A case study from Jordan. *Proceedings Sardinia 2007, Eleventh International Waste Management and Landfill Symposium S. Margherita di Pula, Cagliari, Italy; 1 - 5 October 2007*.
- Qian, L., Zhang, W., Yan, J., Han, L., Gao, W., Liu, R., & Chen, M., 2016. Effective removal of heavy metal by biochar colloids under different pyrolysis temperatures. *Bioresource Technology*. 206, 217–224 <https://doi.org/10.1016/j.biortech.2016.01.065>

- Qiu, Y. P., Cheng, H. Y., Xu, C., and Sheng, G., 2008. Surface characteristics of crop residue derived black carbon and lead II adsorption. *Water Res.* 42: 567 – 574.
- Ra, J. S., Jeong, T. Y., Lee, S. H., & Kim, S. D. 2016. Application of toxicity identification evaluation procedure to toxic industrial effluent in South Korea. *Chemosphere* 143 2016 71 – 77. *Chemosphere*.
<https://doi.org/10.1016/j.chemosphere.2015.05.004>
- Ranade, V. V., and Bhandari, V. M., 2014. *Industrial wastewater treatment, recycling and reuse*. Elsevier Butterworth–Heinemann: UK ISBN: 978-0-08-099968-5
- Rees, F., Simonnot, M. O., and Morel, J. L., 2014. Short-term effects of biochar on soil heavy metal mobility are controlled by intra-particle diffusion and soil pH increase. *European Journal of Soil Science*, 65, 149 – 161.
- Reichman, S. M. 2000. *The Responses of Plants to Metal Toxicity: A Review Focusing on Copper, Manganese and Zinc*. ISBN: 187620513X
- Rieuwerts, J.S., Thornton, I., Farago M.E., and Ashmore, M.R., 1998. Factors influencing metal bioavailability in soils: preliminary investigations for the development of a critical loads approach for metals. *Chemical Speciation & Bioavailability*, 10:2, 61-75, DOI: 10.3184/095422998782775835
- Ro, K.S., Cantrell, K.B., Hunt, P.G., 2010. High-temperature pyrolysis of blended animal manures for producing renewable energy and value-added biochar. *Ind. Eng. Chem Res.* 49, 10125–10131
- Roberts, D. A., and de Nys, R., 2016. The effects of feedstock pre-treatment and pyrolysis temperature on the production of biochar from the green seaweed *Ulva*. *Journal of Environmental Management* 169, 253 – 260.
- Rodda, N., Carden, K., Armitage, N., & Du Plessis, H. M. [2010]. Guidelines for sustainable use of greywater in small-scale agriculture and gardens in South Africa.
- Rodríguez-vila, A. Selwyn-Smith. H., Enunwa, L., Smail, L., Covelo, E. F., and Sizmur, T., 2018 'Predicting Cu and Zn sorption capacity of biochar from feedstock C / N ratio and pyrolysis temperature'. *Environmental Science and Pollution Research*, 25:7730–7739.

- Ronsse, F., van Hecke, S., Dickinson, D., Prins, W., 2013. Production and characterization of slow pyrolysis biochar: influence of feedstock type and pyrolysis conditions. *GCB Bioenergy* 5, 104–115. <http://dx.doi.org/10.1111/gcbb.12018>.
- Rose, C., Parker, A., Jefferson B and Cartmell E., 2015. The characterisation of feces and urine: A review of the literature to inform advanced treatment technology. *Crit. Rev. Env. Sci. Tec.* 45, 1827-1879.
- Ross, D. S., and Ketterings, Q., 2011. Recommended methods for determining soil cation exchange capacity. In: recommended soil testing procedures for the north-eastern united states. Cooperative Bulletin No. 493, 75 – 86.
- Rout, Gyana, Premananda Das, Metal Toxicity, and Metabolism I. Zinc. 2003. "Effect of Metal Toxicity on Plant Growth and Metabolism. *Agronomie*, EDP Sciences, 23 1, pp.3 -11. <10.1051/agro:2002073>. <hal-00885964>
- Saarnio, S., Heimonen, K., and Kettunen, R., 2013. Biochar addition indirectly affects N₂O emissions via soil moisture and plant N uptake. *Soil Biology and Biochemistry*, 58: 99 – 106.
- Sampaio, R. M. M., Timmers, R. A., Xu, Y., Keesman, K. J., and Lens, P. N. L., (2009). "Selective Precipitation of Cu from Zn in a pS Controlled Continuously Stirred Tank Reactor." *Journal of Hazardous Materials* 165(1–3):256–65.
- San, I., and Onay, T. T., 2001. Impact of various leachate recirculation regimes on municipal solid waste degradation. *Journal of Hazardous Materials* B87 2001 259 – 271.
- Sanderson, R. T. 1976 Chemical bonds and bond energy. Academic Press; NY ISBN: 0-12-618060-1
- Seo, S., Aramaki, T., Hwang, Y., and Hanaki, K., 2004. Environmental Impact of Solid Waste Treatment Methods in Korea. *Journal of Environmental Engineering*, 130 1: 81 – 89.
- Shah, B. A. 2009. Archive of SID Sorption isotherms and kinetics of chromium uptake from wastewater using natural sorbent material, 61, 77–90.
- Shi, G. R. and Cai, Q. S., 2009. Cadmium tolerance and accumulation in eight potential energy crops. *Biotechnol.Adv.* 27: 555–561.

- Sika, M. P. and Hardie, A. G. 2014. 'Effect of pine wood biochar on ammonium nitrate leaching and availability in a South African sandy soil'. *European Journal of Soil Science*, 65, 113 – 119. doi: 10.1111/ejss.12082.
- Singh, B. P., Hatton, B. J., Singh, B., Cowie, A. L., and Kathuria, A., 2010. Influence of biochars on nitrous oxide emission and nitrogen leaching from two contrasting soils. *Journal of Environmental Quality* 39, 1224 – 1235. doi:10.2134/jeq2009.0138
- Singh, B., Singh, B. P., and Cowie, A. L. 2010. Characterisation and evaluation of biochars for their application as a soil amendment. In *Australian Journal of Soil Research*, 48: 516 – 525. <https://doi.org/10.1071/SR10058>
- Singh, R. P., and Agrawal, M. 2010. Variations in heavy metal accumulation, growth and yield of rice plants grown at different sewage sludge amendment rates. *Ecotoxicology and Environmental Safety*, 734, 632–641. <https://doi.org/10.1016/j.ecoenv.2010.01.020>
- Singh, R. P., and Agrawal, M. 2010. Effect of different sewage sludge applications on growth and yield of *Vigna radiata* L. field crop: Metal uptake by plant. *Ecological Engineering*, 367, 969–972. <https://doi.org/10.1016/j.ecoleng.2010.03.008>
- Singh, R. P., Singh, P., Araujo, A. S. F., Ibrahim, M. H., Sulaiman, O., 2011. Management of urban solid waste: Vermicomposting a sustainable option. *Resources, Conservation and Recycling*, 55: 719 – 729.
- Smil, V., 1999. Nitrogen in crop production: an account of global flows. *Global Biogeochem. Cy.* 132, 647 – 662.
- Snyman, H. G., Herselman, J. E., and Kasselmann, G., Metal content of South African sewage sludge and an evaluation of the analytical methods for their determination in sludge. *Proceedings of the 2004 Water Institute of Southern Africa WISA Biennial Conference 2 – 6 May 2004 Cape Town, South Africa* ISBN: 1-920-01728-3.
- Sohi, S. P., Loetz-Capel, E., Krull, E., and Boll, R., 2009. Biochar, climate change and soil: A review to guide future research. *CSIRO Land and Water Science Report* 05/09. Canberra: CSIRO.

- Stumpe, J. M., and Vlek, P. L. G., 1991. Acidification Induced by Different Nitrogen Sources in Columns of Selected Tropical Soils. *Soil Sci. Soc. Am. J.* 55:145-151 1991.
- Sweet, H. R., and Fetrow, R. H., 1975. Ground-water pollution by wood waste disposal. *Groundwater*. March – April 1975 Vol 13 2, 227 – 231.
- Taghizadeh-Toosi, A., Clough, T. J., Sherlock, R. R., and Condon, L. M., 2011. A wood-based low-temperature biochar captures $\text{NH}_3\text{-N}$ generated from ruminant urine-N, retaining its bioavailability. *Plant Soil*, 353:73 – 84.
- Taiwo, A. M., 2011. Composting as a sustainable waste management technique in developing countries. *Journal of Environmental Science and Technology* 4 2: 93 – 102
- Tan, X., Liu, Y., Zeng, G., Wang, X., Hu, X., Gu, Y., and Yang, Z., 2015. Application of biochar for the removal of pollutants from aqueous solutions. *Chemosphere*. 125 2015 70 – 85 <https://doi.org/10.1016/j.chemosphere.2014.12.058>
- Tesfamariam, E. H., 2009. Sustainable use of sewage sludge as a source of nitrogen and phosphorus in cropping systems. PhD thesis. University of Pretoria, South Africa.
- Tian, Y., Zhang, J., Zuo, W., Chen, L., Cui, Y., and Tan, T., 2013. Nitrogen conversion in relation to NH_3 and HCN during microwave pyrolysis of sewage sludge. *Environ. Sci. Technol.* 47, 3498 – 3505.
- Trakal, L., Bingol, D., Pohorely, M., Hruska, M., Komarek, M., 2014. Geochemical and spectroscopic investigations of Cd and Pb sorption mechanisms on contrasting biochars: engineering implications. *Bioresour. Technol.* 171, 442–451.
- Trujillo-gonz, J. M., Mahecha-pulido, J. D., Torres-mora, M. A., Brevik, E. C., Keesstra, S. D., & Jim, R. n.d. Impact of Potentially Contaminated River Water on Agricultural Irrigated Soils in an Equatorial Climate, 1–11. <https://doi.org/10.3390/agriculture7070052>
- Trupiano, D., Coccozza, C., Baronti, S., Amendola, C., Vaccari, F. P., Lustrato, G., Di Lonardo, S., Fantasma, F., Tognetti, R., and Scippa, G. S. 2017. The Effects of Biochar and Its Combination with Compost on Lettuce *Lactuca sativa* L.

Growth, Soil Properties, and Soil Microbial Activity and Abundance. Hindawi International Journal of Agronomy Volume 2017, <https://doi.org/10.1155/2017/3158207>

- Turner, P. E. T., Wood, R. A., and Meyer, J. H., 1991. Investigation into the use of sewage sludge as a soil amendment for sugarcane. Proceedings of the South African Sugar Technologists Association – June 1991.
- Uchimiya, M., Chang, S., & Klasson, K. T. 2011. Screening biochars for heavy metal retention in soil: Role of oxygen functional groups. Journal of Hazardous Materials. <https://doi.org/10.1016/j.jhazmat.2011.03.063>
- Uchimiya, M., Lima, I. M., Klasson, K. T., and Wartelle, L. H., 2010. Contaminant immobilization and nutrient release by biochar soil amendment: Roles of natural organic matter. Chemosphere 80, 935 – 940.
- United States Department of Agriculture, 2002. Successful approaches to recycling urban wood waste. Solid Waste Association of North America. Applied Research Program. Silver Spring, Maryland.
- van Zwieten, L., Kimber, S., Morris, S., Chan, K. Y., Downie, A., Rust, J., Joseph, S., and Cowie, A., 2010. Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. Plant Soil 327: 235 – 246.
- Vaughan, S. F., Dinelli, F. D., Tisserat, B., Joshee, N., Vaughan, M. M., and Peterson, S. C., 2015. Creeping bentgrass growth in sand-based root zones with or without biochar. Scientia Horticulturae 197, 592 – 596.
- Vinneras, B., Palmquist, H., Balmer, P., and Jonsson, H., 2006. The composition of household wastewater and biodegradable solid waste proposal for new norms for the flow of nutrients and heavy metals. Urban Water 3 1 3 - 11.
- Vodounhessi, A., and von Munch, E., 2006. Financial Challenges to Making Fecal Sludge Management an Integrated Part of the Ecosan Approach: Case Study of Kumasi, Ghana. Water Practice & Technology Vol 1 No 2 © IWA Publishing 2006 doi: 10.2166/WPT.2006045.
- Wagner, A., and Kaupenjohann, M., 2014. Suitability of biochars pyro- and hydrochars for metal immobilization on former sewage-field soils. European Journal of Soil Science, 65, 139 – 148.

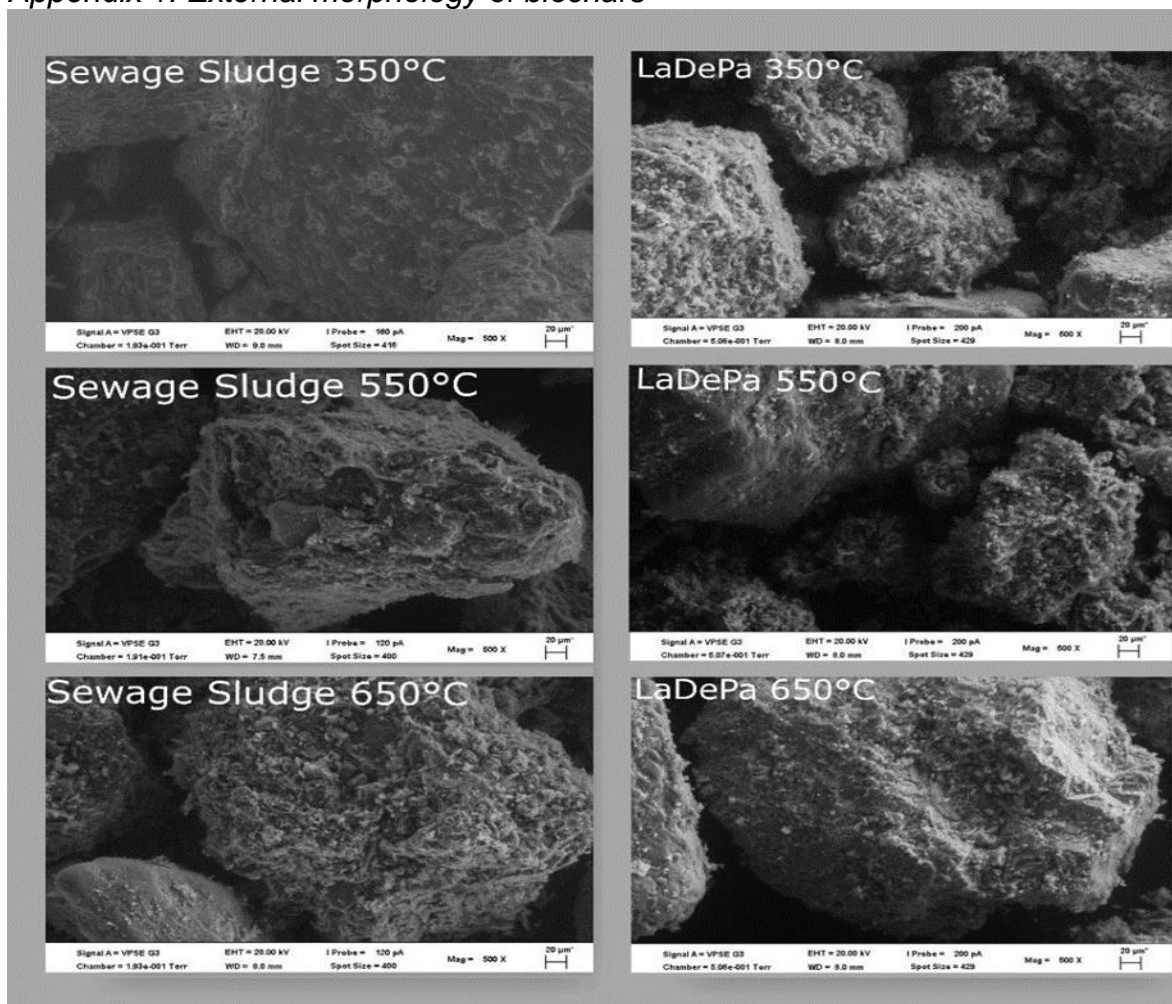
- Walker, D. J., Clemente, R., Roig, A., and Bernal, M. P., 2003. The effects of soil amendments on heavy metal bioavailability in two contaminated Mediterranean soils. *Environmental Pollution* 122 2003 303 – 312.
- Walker, D.J., Clemente, R., and Bernal, M. P., 2004. Contrasting effects of manure and compost on soil pH, heavy metal availability and growth of *Chenopodium album* L. in a soil contaminated by pyritic mine waste. *Chemosphere* 57, 215 – 224.
- Wan, Q., Yuan, J., Xu, R and Li, X., 2014. Pyrolysis temperature influences ameliorating effects of biochars on acid soil. *Environ Sci Pollut Res* 21, 2486 – 2495.
- Wang, L., Weller, C. L., Jones, D. D., and Hanna, M. A., 2008. Contemporary issues in thermal gasification of biomass and its application to electricity and fuel production. *Biomass Bioenerg.* 32, 573 – 581.
- Wang, S., Gao, B., Zimmerman, A. R., Li, Y., Ma, L., Harris, W. G., Migliaccio, K. W., 2015. Removal of arsenic by magnetic biochar prepared from pinewood and natural hematite. *Bioresour. Technol.* 175, 391 – 395.
- Watson, R. T., and Zakri, A. H., 2008. Living beyond our means. Natural assets and human well-being. Statement from the Board. Millenium Ecosystem Assessment.
<http://www.millenniumassessment.org/documents/document.429.aspx.pdf>
- Wei, X., Hao, M., Shao, M., and Gale, W., J., 2006. Changes in soil properties and the availability of soil micronutrients after 18 years of cropping and fertilization. *Soil & Tillage Research* 91, 120–130
- Winblad, U., and Simpson-Hebert, M., 2004. Ecological sanitation. Stockholm Environment Institute, Sweden. ISBN 91-88714-98-5.
- Wong, B. Y. M. H. and A. D. Bradshaw., 1982. A comparison of the toxicity of heavy metals, using root elongation of ryegrass, *Lolium Perenne*. *New Phytol.* 1982 91; 255 - 261.
- World Health Organisation, 2006. WHO guidelines for the safe use of wastewater, excreta and greywater: Volume 1 policy and regulatory aspects. WHO Press and United Nations Environmental Programme.

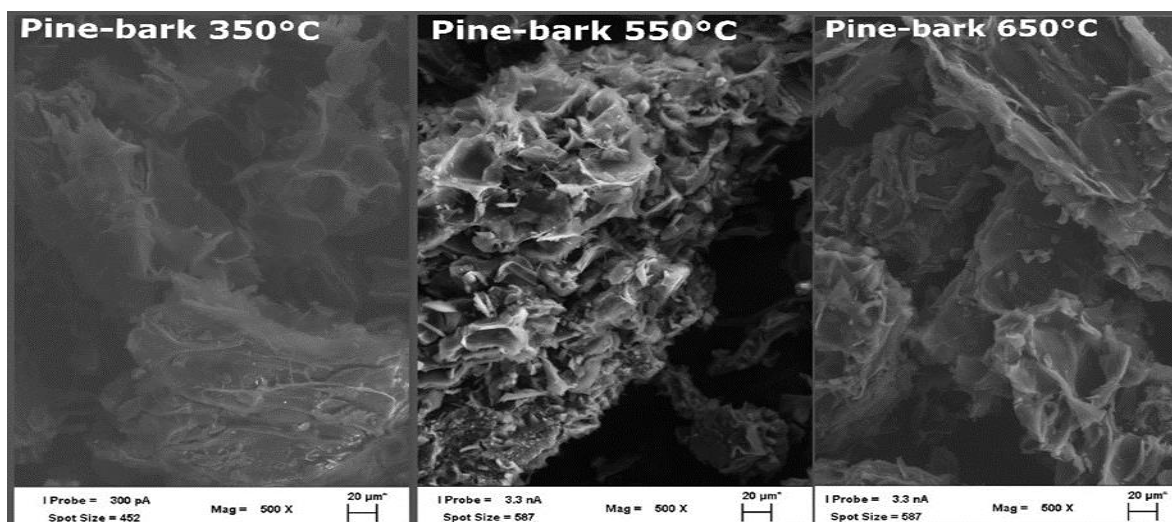
- Wu, W., Yang, M., Feng, Q., McGrouther, K., Wang, H., Lu, H., and Chen, Y., 2012. Chemical characterization of rice straw-derived biochar for soil amendment. *Biomass and Bioenergy*, 47: 268 – 276.
- Xu, X., Cao, X., & Zhao, L., 2013. Comparison of rice husk- and dairy manure-derived biochars for simultaneously removing heavy metals from aqueous solutions: Role of mineral components in biochars. *Chemosphere* 92, 955–961 <https://doi.org/10.1016/j.chemosphere.2013.03.009>
- Xu, X., Cao, X., Zhao, L., Wang, H., Yu, H., & Gao, B., 2013. Removal of Cu, Zn, and Cd from aqueous solutions by the dairy manure-derived biochar. *Environmental Science and Pollution Research*, 20:358–368 <https://doi.org/10.1007/s11356-012-0873-5>
- Xu, Y., and Chen, B., 2014. “Organic Carbon and Inorganic Silicon Speciation in Rice-Bran-Derived Biochars Affect Its Capacity to Adsorb Cadmium in Solution.” *Journal of Soils and Sediments*. *J Soils Sediments* 2015 15:60–70 DOI 10.1007/s11368-014-0969-2
- Yan-chao, B., Chuan-hui, G., Tian-yun, T., Xiao-wen, Z., Yi-ran, X., Yu-hua, S., and Ke, F., 2014. Responses of ryegrass *Lolium perenne* grown in mudflats to sewage sludge amendment. *Journal of Integrative Agriculture*, 13 2: 426 – 433.
- Yesil-Celiktas, O., Ganzera, M., Akgun, I., Sevimli, C., Korkmaz, K. S., and Bedir, E., 2009. Determination of polyphenolic constituents and biological activities of bark extracts from different *Pinus* species. *J SCI Food Agric*, 89: 1339 – 1345.
- Yuan, H., Lu, T., Huang, H., Zhao, D., Kobayashi, N., and Chen, Y. Y., 2015. Influence of pyrolysis temperature on physical and chemical properties of biochar made from sewage sludge. *Journal of Analytical and Applied Pyrolysis* 112, 284 – 289.
- Yuan, J. H., Xu, R. K., and Zhang, H., 2011. The forms of alkalis in the biochar produced from crop residues at different temperatures. *Bioresour Technol* 102, 3488 – 3497.
- Yuan, J.-H., and Xu, R.-K., 2011. The amelioration effects of low-temperature biochar generated from nine crop residues on an acidic ultisol. *Soil Use and Management*, 27:110 – 115.

- Zhang, M., Gao, B., Varnoosfaderani, S., Hebard, A., Yao, Y., Inyang, M., 2013. Preparation and characterization of a novel magnetic biochar for arsenic removal. *Bioresour. Technol.* 130, 457–462.
- Zhang, W., Huang, X., Jia, Y., Rees, F., Daniel, C. W., Qiu, R., Rees, F., and Wang, H. 2017. Metal immobilization by sludge-derived biochar: roles of mineral oxides and carbonized organic compartment To cite this version : HAL Id : hal-01458427 Metal immobilization by sludge-derived biochar: roles of mineral oxides and carbonized organic compar. *Environmental Geochemistry and Health*. <https://doi.org/10.1007/s10653-016-9851-z>
- Zhou, G., Luo, J., Liu, C., Chu, L., Ma, J., Tang, Y., and Luo, S., 2016. A highly efficient polyampholyte hydrogel sorbent based fixed-bed process for heavy metal removal in actual industrial effluent. *Water Research* 89, 151 – 160 <https://doi.org/10.1016/j.watres.2015.11.053>
- Zhou, Q., 2003. Interaction between heavy metals and nitrogen fertilizers applied to soil-vegetable systems. *Bulletin of Environmental Contamination and Toxicology*, 71: 338 – 344.
- Zimms, M., and Barrett, S., [2004]. Managing industrial wood waste: Sumter county wood refuse and exchange centre. Managing industrial wood waste: building blocks to proper disposal. Kessler Consulting Inc. Tampa, Florida, USA.

APPENDICES

Appendix 1: External morphology of biochars





Appendix 2: Freundlich parameters of Zn, Cu and Cr on biochars whose Langmuir model did not fit.

Biochar	K	$\frac{1}{n}$	R ²
<i>Zn effluent</i>			
LW 550	0.0027	0.8124	0.94
LW 650	0.0293	0.5047	0.97
SS 550	0.0518	0.3773	0.81
SS 650	0.0029	0.6624	0.99
<i>Cu single metal solution</i>			
LW 350	0.0082	0.7286	0.99
SS 350	46.036	1.3486	0.99
PB 350	39.756	0.2460	1.00
<i>Cr effluent</i>			
LW 350	116.01	1.021	0.94
SS 350	44.822	0.572	0.92
PB 350	21.399	1.037	0.99

LW = latrine waste biochar, SS = sewage sludge biochar, PB = pine-bark biochar