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**POTENTIAL OF BIOCHAR FROM PHYTOREMEDIATION
BIOMASSES FOR THE REMOVAL OF IONIC CONTAMINANTS
FROM WASTEWATER**

By

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Declaration Regarding the Work and Copyright

DECLARATION REGARDING THE WORK AND COPYRIGHT

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Thesis Titled: **Potential of Biochar from Phytoremediation Biomasses for the Removal of Ionic Contaminants from Wastewater**

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Abstract

There is a challenge regarding the disposal and handling of post-harvested phytoremediation biomass, but one alternative process is to convert phytoremediation biomass into biochar and bioenergy by pyrolysis. This study aims at utilizing biochar derived from phytoremediation biomasses to remove ionic contaminants from wastewater. Phytoremediation and non-phytoremediation biomasses were pyrolyzed at 550°C in a nitrogen-flowing environment for 30 minutes and the properties were analyzed and compared. The resultant biochar was valorized using 0.1 M Zinc chloride (ZnCl_2) and adsorption experiments were performed.

Phytoremediation biomasses had higher heavy metal (HMs) content compared to phytoremediation biomasses and the carry-over effect was observed in subsequent biochars. Generally, biochars from phytoremediation biomasses displayed higher ash content, and volatile matter content but had low fixed carbon (FC), pH, and electrical conductivity (EC). The biplot indicated an increase in identified functional groups from non-phytoremediation biochars to phytoremediation biochars except for *Cymbopogon citratus* (*C. citratus*). Biochars from *Chrysopogon zizanioides* (*C. zizanioides*) phytoremediation biochars showed low intensities of anatase and dolomite peaks. Biochars from phytoremediation biomasses have fewer porous structures as compared to biochars from non-phytoremediation biomasses. ZnCl_2 -activation did not alter the ordinary surface functional group profiles but increased the ordinary biochar's surface porosity. The activation of ordinary biochars with ZnCl_2 reduced the magnitude of the potential positive charges that can develop and adsorb anions. Generally, phytoremediation biochars indicated negative adsorption capacities suggesting that heavy metals in biochars leached into the AMD solution.

Abstract

The activated phytoremediation biochar from *Chrysopogon zizanioides* (*C. zizanioides*) indicated the highest adsorption capacity of 14.12 mg g^{-1} for PO_4^{3-} ion at a biochar dosage of 0.04 g while *Cymbopogon nardus* retained 20.72 mg g^{-1} of NO_3^- ion. Based on the effect of pH on adsorption, activated non-phytoremediation biochar from *Cymbopogon nardus* (*C. nardus*) showed the maximum adsorption capacities of 38.93 mg g^{-1} and 31.52 mg g^{-1} for PO_4^{3-} and NO_3^- ions, respectively at pH 8. Based on the effect of initial concentration on adsorption, ordinary non-phytoremediation biochar from *Cymbopogon nardus* effectively retained 69.06 mg g^{-1} of PO_4^{3-} ion at the initial concentration of 300 mg l^{-1} . The maximum adsorption capacities for PO_4^{3-} that can be reached by *Chrysopogon zizanioides* non-phytoremediation biochar (BCV1), *Chrysopogon zizanioides* phytoremediation biochar (BCV2), activated BCV1, activated BCV2 and activated *Cymbopogon nardus* phytoremediation biochar (BCC2) are 62.99 , 72.99 , 113.64 , 115.70 and 61.38 mg g^{-1} , respectively. In conclusion, the biochar from phytoremediation biomasses showed high potential as an adsorbent for the anionic contaminants in wastewater.

Keywords: Bioaccumulation, translocation, pyrolysis, decomposition, devolatilization, biochar, morphology, crystallization, valorization, adsorbate, adsorbent, adsorption, and isotherm.

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List of Abbreviations

AC	Activated
Ana	Anatase
Anova	Analysis of variance
Ant	Antigorite
AMD	Acid mine drainage
BC	Biochar
BCC1	<i>Cymbopogon nardus</i> non-phytoremediation biochar
BCC2	<i>Cymbopogon nardus</i> phytoremediation biochar
BCL	Bamangwato Concession Limited
BCL1	<i>Cymbopogon citratus</i> non-phytoremediation biochar
BCL2	<i>Cymbopogon citratus</i> non-phytoremediation biochar
BCV1	<i>Chrysopogon zizanioides</i> non-phytoremediation biochar
BCV2	<i>Chrysopogon zizanioides</i> non-phytoremediation biochar
BOD	Biological oxygen demand
Cal	Calcite
CEC	Cation exchange capacity
Cor	Corrondium
Chr	Chrysotile
Dol	Dolomite
EC	Electrical conductivity
FC	Fixed carbon
FTIR	Fourier-transformer infrared spectroscopy
Gei	Geikielite
Heu	Heulandite
HM	Heavy metal
IC	Ion Chromatography
ICP-OES	Inductively coupled plasma-optical emission spectrometry
LG	Langmuir
Pzc	Point of zero charge
Qeh	The highest equilibrium adsorption capacity
Qua	Quartz
SEM	Scanning electron microscope
Sph	Sphalerite
Tal	Talc
VM	Volatile matter
Xrd	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1. Background Information

Phytoremediation involves the utilization of plants for the adsorption of contaminants from polluted soil or water. Recently, phytoremediation as a cost-effective and green technology has caught the attention of many scientists due to its potential to remediate contaminated soil and water bodies notably acid mine drainage (Lee, 2013). Phytoremediation biomass has the potential to purify the indoor air by removing air contaminants such as O₃, NO_x, CO₂, and SO₂ present in the air (Ravindra and Mor, 2022; Agarwal *et al.*, 2019; Lee, *et al.*, 2021). Despite the potential of phytoremediation biomass to remediate contaminated environments, there are issues associated with its usages such as heavy metal contents and the high probability to transfer pollution (Dražić *et al.*, 2017). Accumulation of heavy metals in phytoremediation plants is also a big concern as these plants provide an exposure pathway for the entry of toxic substances i.e., heavy metals into the food chain when herbivores feed on these biomasses. Phytoextraction of heavy metals is still a threat to the environment since microorganisms cannot degrade toxic metals as such heavy metal-contaminated biomass needs proper handling (Vocciante *et al.*, 2019). Alternatives to phytoremediation biomass disposal include direct disposal, composting, compaction, leaching, incineration, and pyrolysis.

One of the available technologies for handling phytoremediation biomass is by converting the biomass into biochar via the pyrolysis process (He *et al.*, 2019). Biochar is a solid carbon-rich product of pyrolysis that can be generated from different feedstocks such as forest

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remains, industrial wastes, grass, and unordinary materials like papers, bones, and waste tires (Inyang *et al.*, 2016). Biochar yield and chemical attributes mainly rely on the type of biomass and pyrolysis process (Pandey *et al.*, 2020). Different grass species have different quantities of organic constituents such as cellulose, hemicellulose, and lignin which affect the distributions of pyrolytic products (char, gases, bio-oil, and tar) The heavy metal content of biomass may influence the chemical properties of biochar (Zeng *et al.*, 2020). After pyrolysis of phytoremediation biomass at low temperatures, heavy metals are enriched in the biochar while syngas and liquid (bio-oil and tar) will comprise low heavy metal concentrations (Zeng *et al.*, 2019).

Characteristics of biochar such as porous structure, large surface area, and surface functional groups can be applied as an adsorbent of ionic contaminants in wastewater (e.g. acid mine drainage (Tan *et al.*, 2015)X. Li *et al.*, 2020). Acid mine drainage (AMD) is defined as heavy metals and sulfate-bearing water with low pH formed when sulfide mineral rock gets exposed to an oxidizing environment (Gerhardt, 2005). Interaction of acid mine drainage with surface water results in elevated metal concentrations of surface water. An increase in hydrogen ions due to heavy metals in AMD decreases water and soil pH (Farsad and Goldsmith, 2016). The retention and solubility of heavy metals in soil and groundwater are mainly controlled by pH (Orhue and Frank, 2011). Elevated heavy metal concentrations entail more protons which neutralize bicarbonate and carbonate ions resulting in the formation of carbonic acid thus destroying the bicarbonate buffering capacity of a certain water body (Talukdar *et al.*, 2017). The destruction of the bicarbonate buffering system of river water increases the level of carbon dioxide (CO₂) which is unfavorable for aerobic aquatic organisms such as fish. In recent years, the excessive amount of phosphorus and nitrogen compounds in water has become a serious

threat worldwide as it results in water pollution. The main sources of phosphates and nitrates in natural water bodies are households, industrial and agricultural activities (Haghseresht *et al.*, 2009). Eutrophication in aquatic environments can be related to excessive amounts of phosphates and nitrates (Olgun, *et al* 2013).

The adsorption of ionic contaminants in wastewater by adsorbents involves physical and chemical processes (Xia *et al.*, 2019). Physical adsorption involves the attachment of ionic contaminants into the porous structure of the adsorbent via physical interactions while chemical adsorption involves the chemical complexation and precipitation of ionic contaminants with the adsorbent (Xia *et al.*, 2019). Adsorption mechanisms by several adsorbents involve precipitation, electrostatic attraction, surface complexation, ion exchange, and van der Waals forces between adsorbent and adsorbate (Zhang *et al.*, 2020). The sorption of ions by adsorbent is affected by several factors such as solution pH, adsorbent dosage, contact time, temperature, and competing ions (Iftekhar *et al.*, 2018; Al-Ghouti *et al.*, 2010).

1 .2 Problem Statement

The conceptual model of the research problem is presented in Figure 1.1. Mine tailings, as one of the mine wastes of metal mines such as BCL mine tend to discharge acidified water into areas adjacent to the mines which result in environmental impacts such as destruction of vegetation cover, soil infertility, and death of sensitive organisms. As a solution, scientists have employed the use of phytoremediation technology to rehabilitate heavy metals contaminated water and soil bodies but up to date, there is still a challenge with the utilization and proper disposal of phytoremediation biomasses. Incineration of phytoremediation biomass could result in the volatilization of heavy metals into the atmosphere and the metals will freely participate in

secondary chemical reactions e.g., hydrolysis reaction leading to the generation of acid rain during rainy seasons which has detrimental effects on both environment and biotic organisms. Compaction of the phytoremediation biomass produces leachate concentrating heavy metals complex-ed with chelators in bioavailable forms, leakage of the leachate into the environment results in negative impacts such as acidification of surface and groundwater. This study seeks to convert phytoremediation biomasses into biochar and utilize the resultant biochar as a sorbent of ionic contaminants.

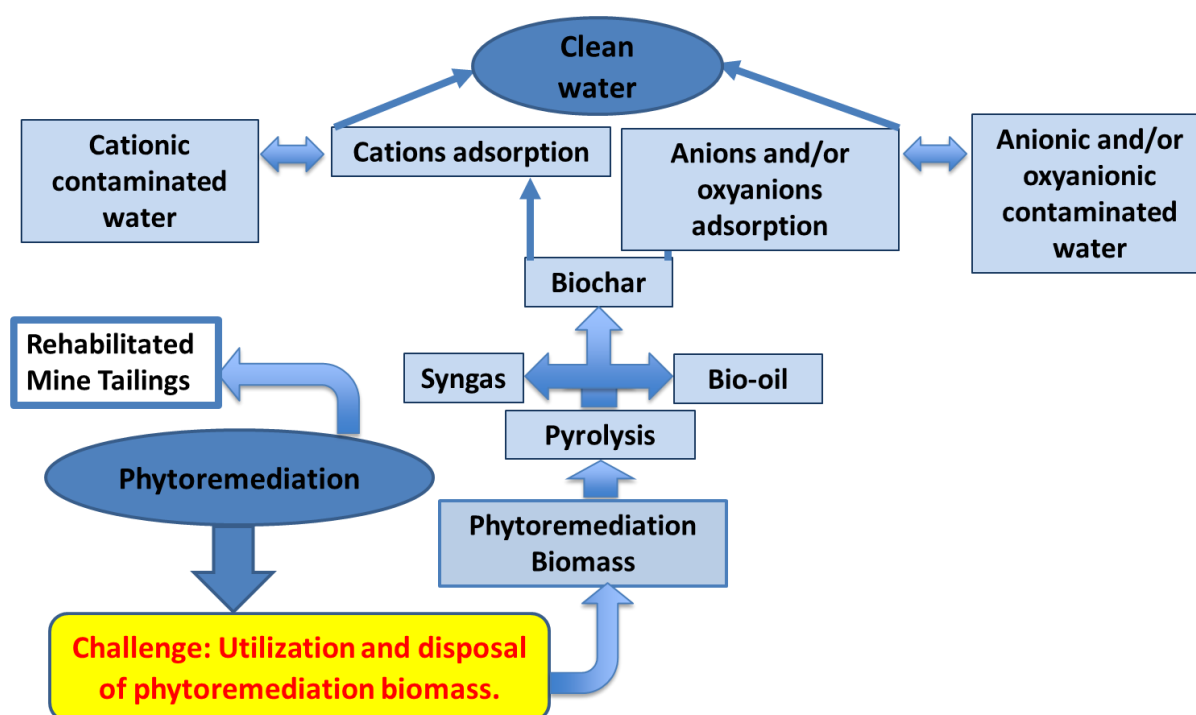


Figure 1.1: Conceptual model of the research problem.

1.3 Research aims and objectives

The main aim of this study is to remove ionic contaminants in wastewater using biochar derived from phytoremediation biomass.

Introduction

Specific Objectives:

- a) To characterize the physicochemical properties of phytoremediation and non-phytoremediation biomasses and subsequent biochars produced by pyrolysis.
- b) To valorize phytoremediation biochar using 0.1M zinc chloride and assess its physicochemical properties.
- c) To assess the potential of valorized phytoremediation biochars towards the adsorption of ionic contaminants from wastewater.

1.4 Justification of the Study

This study is undertaken to provide an alternative method for the utilization of phytoremediation biomasses. This project will produce valorized phytoremediation biochar as a sorbent to remove ionic contaminants in wastewater.

1.5 Hypotheses

Biochars from non-phytoremediation and phytoremediation biomasses and their activated forms will differ in the physicochemical properties and absorption capacities for ionic contaminants.

CHAPTER 2

LITERATURE REVIEW

2.1 Characteristics of phytoremediation biomass

This section describes the influence of heavy metals on the chemical composition of grass biomasses.

2.1.1 Heavy metal concentrations of phytoremediation biomass

Generally, phytoremediation biomasses have higher heavy metal concentrations as compared to non-contaminated biomasses (He *et al.*, 2019). Mechanisms of heavy metal phytoremediation involve phytoextraction, phytostabilization, phytodegradation, rhizofiltration, and phytovolatilization (Muthusaravanan *et al.*, 2018). The bioaccumulation of heavy metals by phytoremediation biomasses relies on the intensity of exchangeable metals in the soil, exchangeable and carbonate-bound heavy metal fractions are more available compared to other fractions (Khan *et al.*, 2015). The soil type and solubility influence the uptake of metals by plants (Castro, *et al.*, 2009). Plants with the changed structure and defense mechanisms have better tolerance for heavy metals (Yuan *et al.*, 2019).

2.1.2 Essential nutrient concentrations of phytoremediation biomass

Heavy metal content of phytoremediation biomass strongly causes a nutritional deficiency in plant species (Bakht, *et al.*, 2016). The presence of heavy metals such as cadmium adsorbed by membrane transporters of essential elements can disrupt the uptake, transport, and function of some elements. Heavy metals turn to interfere with enzyme activity and ionic

equilibrium which affects physiological processes such as root nutrient uptake of single organs(Kumar *et al.*, 2019).

2.1.3 Lignin, cellulose, and hemicellulose content of phytoremediation biomass

Accumulation of substances such as heavy metals in plants may alter their structural compounds such as lignin, cellulose, and hemicellulose contents (Waliszewska *et al.*, 2019). Alteration of these compounds could reduce the biomass increment and morphological characteristics of the plant. Liu, *et al.*, (2018) reported that the phenolic secondary metabolic synthesis pathway could be stimulated by heavy metal leading to an increase in lignin content thereby improving cell wall thickness.

2.2 Management and utilization of phytoremediation biomasses

Post-harvested phytoremediation biomass consists of heavy metals which pose a threat to the environment (Ghosh and Singh, 2005). Scientists proposed incineration, compaction, pyrolysis composting, direct disposal, and leaching as some of the technological options for managing and utilizing phytoremediation biomass.

2.2.1 Incineration

It involves the thermal decomposition of organic materials and phytoremediation biomass at elevated temperatures. Ghosh and Maiti (2021), reported that incineration of phytoremediation biomass is the best method for recovery of Pb, Zn, and Ni. Most countries embraced the incineration method as a way of handling phytoremediation biomass because of the reliability of the method and volume minimization of the biomass (Wijekoon *et al.*, 2021).

The disadvantage of this method is that some of the heavy metals may be volatilized together with the flue gas and the disposal of fly ash concentrating heavy metals becomes a concern.

2.2.2 Compaction

The compaction process involves the subjection of phytoremediation biomass to high pressure which releases leachate to be disposed of (Sas *et al.*, 2004). The container for compaction must have a press and leachate collection system. Leachate from phytoremediation biomass contains high heavy metal concentrations complexed with chelators in both bioavailable Compaction requires a short time compared to composting for the same plant biomass (Fu, *et al.*, 2021). Immediately after the collection of leachates, heavy metals in leachate must be treated otherwise the metals will find a pathway into the environment leading to an increase in treatment cost.

2.2.3 Pyrolysis

It is a process that involved the thermal decomposition of biomass in an inert environment (Vocciante *et al.*, 2019). Pyrolysis can be classified into 3 categories: slow, fast, and flash pyrolysis (Tripathi, *et al.*, 2016; Elkhailifa *et al.*, 2019; Al-Rumaihi *et al.*, 2022). Slow pyrolysis of the biomass is opted for obtaining biochar at a temperature range of 400 and 500 °C and residence time between 5 and 30 minutes within a heating rate of about 0.1 to 1°C/s (Tripathi *et al.*, 2016). Fast pyrolysis involves the decomposition of the biomass in an inert environment at a temperature range of 850 to 1250 °C, for a short period (1 to 10 seconds) to produce high-quality bio-oil (Bridgwater, 2003). Flash pyrolysis is an improved version of fast pyrolysis, flash

pyrolysis entails the heating of the raw biomass at a higher rate of the order 1000 °C/s within a temperature range of 900 to 1200°C for a short residence time of 0.1-1 second (Li *et al.*, 2013).

The by-products of biomass pyrolysis include biochar (solid fraction), liquids, and syngas. Technically, pyrolysis has been evaluated and confirmed as a sustainable method for the post-treatment of phytoremediation biomass. Pyrolysis helps in the reduction of phytoremediation biomass and water content (Sas *et al.*, 2004). Heating phytoremediation biomass at low temperatures prevents volatilization of heavy metals which better controls their fate (Chai *et al.*, 2022). The disadvantage of pyrolysis of phytoremediation biomass is that there is limited potential to produce energy because the bio-oil has a low calorific value.

2.2.3.1 Pyrolysis mechanisms

The pyrolysis process is comprised of two mechanisms: the primary and secondary mechanisms (Al-Rumaihi *et al.*, 2022). The primary mechanism involves the disintegration of the chemical bonds of the feedstock to release the volatile compounds in the reactor subjected to heat, which will further undergo secondary reactions (Van de Velden *et al.*, 2010). In the first stage of the thermal degradation of the biomass, benzene rings form and combine to form bio-charcoal residue together with organic matter which can be further decomposed up to 800 °C. The decomposition process transforms the long polymer chains of organic matter into small monomers resulting in the release of water, incondensable gas, oils, and tars (McGrath, *et al.*, 2003; Aravind *et al.*, 2020).

The small-chain organic compounds and incondensable gasses are formed because of the association of covalent bonds in the monomers (Al-Rumaihi *et al.*, 2022). Secondary mechanisms include the reconstruction of unstable compounds either by cracking or

recombination. Unstable compounds decompose to form low molecular weight during cracking while recombination entails the formation of high molecular weight as a result of a combination of unstable compounds. In some cases, the secondary mechanism can produce bio-charcoal (Hosoya, *et al.*, 2007). The solid by-product of the pyrolysis process is known as biochar, which contains char, untransformed biomass structure, and ash content (Angin, 2013).

2.2.3.2 Advantages and disadvantages of pyrolysis

The advantage of pyrolysis is that metals contained in ash content after pyrolysis are not oxidized hence they have a higher commercial use (Miteva, 2019). Pyrolysis highly reduces the volume of biomass as compared to incineration (Miteva, 2019). Small land is required for the installation of pyrolysis reactors (Malkow, 2004). The main setback regarding pyrolysis is that pyrolysis products are further treated before their disposal which increased the costs of using the pyrolysis technique (Chen *et al.*, 2014).

2.2.4 Composting

This process involves the decomposition of organic compounds by aerobic microorganisms e.g., thermophilic, and mesophilic microorganisms, and the end product is called compost (Wijekoon *et al.*, 2021). During the first step of composting, there is a change in pH due to acidic formation due to the organic decomposition of biomass (Singh and Kalamdhad, 2012). The compost of phytoremediation biomass will consist of heavy metals assimilated to crystal structures of primary and secondary minerals. The process of oxidation and organo-metallic complexes formation occurring during decomposition at the thermophilic phase could minimize the soluble content of metals (He, *et al.*, 2009). Humic substances attach to the

carbonate and exchangeable fragments of heavy metals. Composting reduces the volume of the phytoremediation biomass but there is a need for pre-treatment of the biomass before its disposal.

2.2.5 Direct disposal

The treatment option for phytoremediation biomass involves direct disposal of the biomass into the landfill (Quarshie *et al.*, 2021). The advantage of this post-treatment is that it is easy to operate and time-saving. Direct disposal of phytoremediation biomass is not recommended since the chemical composition of the biomass concentrates heavy metals which exhibit toxic effects on the terrestrial environment. The leachate from phytoremediation biomass must be consistently monitored and tested for solubility and leaching of heavy metals.

2.2.6 Leaching

Percolation of water drains soluble metals from decomposed phytoremediation biomass which makes it a hazardous waste (Kovacs and Szemmelveisz, 2017). Leachate of heavy metals can be obtained by treating the compressed biomass with solvents such as water. Leaching offers an opportunity for heavy metals recovery and the disposal of the biomass residuals is easier (Sas *et al.*, 2004). The main disadvantage of phytoremediation biomass leaching is that additional treatment of the biomass and percolate is required. Generally, it is expensive to recover metals from leached solutions.

2.2 Influence of crystalline minerals on biochar properties

The alkaline nature of biochar is due to its mineral constituents (Vijayaraghavan, 2021). The high ash content of biochar correlates to its high mineral constituents which could decrease biochar's specific surface area and pore volume. Improvement of biochar's surface area can be achieved by de-ashing of rich-ash content biochar. According to the study conducted by (Zhao *et al.*, 2015), the point of zero charges of biochar derived from solid waste was higher than that of biochar produced from plant residues relating to the high mineral content of biochar from solid waste.

2.4 Prospects and challenges in Phytoremediation biomass utilization

There is limited information on the physicochemical characteristics of phytoremediation biomasses and phytoremediation biochars. There is scarce information on the effects of biochar inherent metals on biochar physicochemical characteristics. Most of the studies have been conducted on the adsorption of heavy metals from either synthetic acid water or acid mine drainage using biochars derived from various feedstocks but there is still missing information on the utilization of activated phytoremediation biochars to adsorb heavy metals from acid mine drainage.

2.5 Biochar Activation using ZnCl_2

Biochar activation is the process of increasing adsorption sites or capacity of biochar either by physical, thermal, or chemical mechanisms (Gámiz *et al.*, 2019). Physical activation involves ball milling and grinding of biochar, chemical activation involves the treatment of biochar with oxidizers, acids, or bases while thermal activation is whereby biochar

is re-pyrolyzed at an elevated temperature than the actual product temperature. The main aim of biochar valorization is to induce reactive functional groups and to enhance the specific surface area of biochar (Borchard *et al.*, 2012). The low melting point (283-293 °C) of ZnCl_2 enables it to have easier contact with the carbon surface at an activation temperature above 500 °C (Li *et al.*, 2020). Activation with ZnCl_2 destroys the cellulosic material and penetrates macropores, causing charring and aromatization of carbon structure which results in the formation of micropore structures (Olivares *et al.*, 2006; Ding *et al.*, 2021).

2.6 Impacts of acid mine drainage

The biological oxygen demand refers to the amount of oxygen needed by microbes such as bacteria and fungi to decompose organic material under an oxygen environment (Banerjee *et al.*, 2016). Heavy metals such as Fe^{2+} , Cd^{2+} , Ni^{2+} , and Cu^{2+} in AMD alter the respiration rate of certain microorganisms such as *Bacillus subtilis* which participate in organic matter decomposition (Kwok *et al.*, 2005). Gomaa *et al.*, (2020) reported that an increase in Pb and Cu concentrations in soil decreases soil electrical conductivity while an increase in Mn, Zn, and Ni increases the conductivity of the soil. Heavy metals inhibit plant growth; Cu disrupts reproduction and photosynthesis processes while Pb decreases chlorophyll production (Rambabu *et al.*, 2020). Acid mine drainage causes the death of animals and plants which ultimately disturbs wildlife habitat and decreases vegetation cover in areas within the vicinity of metal mines (Samal *et al.*, 2020).

2.7 Effects of phosphates and nitrates

The excessive concentrations of nitrates and phosphates in water bodies usually promote algal bloom (eutrophication) (Wang *et al.*, 2016). The eutrophication results in oxygen depletion and kills aquatic species such as fish (Karthikeyan and Meenakshi, 2019). It has been reported that human illnesses such as nitrosamine, baby syndrome, and infant methemoglobinemia are caused by the presence of nitrates in drinking water (Eltaweil *et al.*, 2021).

2.8 Biochar adsorption mechanisms

Adsorption of contaminants such as heavy metals from wastewater by biochar is achieved by physical and chemical means. Physical adsorption entails the diffusional movement of metallic ions into the porous structure of the biochar without the formation of chemical bonds (Inyang *et al.*, 2016). Chemical adsorption/chemisorption involves electron sharing between adsorbate and adsorbents which forms either an ionic or covalent bond. Electrostatic adsorption, co-precipitation, complexation, and ion exchange are general adsorption mechanisms of biochar in soil systems (Barquilha and Braga, 2021). The pore spaces of the biochar provide attachment sites for heavy metals in the biochar matrix. Heavy metals in the solution get directly immobilized by processes such as complexation (Version, 2019). In multi-heavy metal component systems, cation exchange capacity (CEC) and complexation have been identified as the main two adsorption mechanisms.

2.8.1 Electrostatic adsorption

This involves the attachment of the unlike charge of the adsorbate and the functional groups of the biochar to each other. The negatively charged ions of the biochar

surfaces enable the attachment of positively charged metals onto the surface of biochar due to electrostatic force/effect and vice versa (Abbas *et al.*, 2018).

2.8.2 Ion Exchange

This involves the exchange of the positive ions in solution with the protons on the matrix of the biochar. The process of cation exchange highly depends on the size of the contaminant and the functional groups on the biochar matrix (Abbas *et al.*, 2018). Ionic radii, bond characteristics, and charge differences are very pivotal during the exchange process. Greater potential for adsorption of HMs depends on the high CEC value of the biochar.

2.8.3 Complexation

This is a process whereby complexes form from coordinating ions, atoms, and/or a set of ligands (Mohan *et al.*, 2007). Carboxyl groups form due to an increase in oxygenation of the surface of the biochar which increases the oxygen content of the biochar. Metal complexation increases as oxygen content increases with time.

2.8.4 Co-precipitation

Precipitation of metal sulfides is a crucial process during the treatment of effluents and ores in the hydro-metallurgical industry (Outlooks, 2021). Biochar comprises mineral compounds that dissolve and release anions such as OH^- and CO_3^{2-} which participate in the co-precipitation of heavy metal ions. The precipitation of Heavy metals is driven by the hydration and dissolution of fly ash, CO_2 , and CaO , and metal speciation forms. The dissolution of fly ash occurs in NaOH

and the reaction activity can be accelerated by elevated temperatures (Kuenzel and Ranjbar, 2019).

2.9 Factors affecting adsorption performance

2.9.1 Particle Size of biochar

Particle size affects the removal capacity of HMs, the smaller particle sizes the larger the surface area (Leng *et al.*, 2021). A large surface area corresponds to high surface energy of biochar and the adsorption process also tends to increase with an increase in surface area. The dispersion path for HM ions becomes short in the small biochar particles which gives the ions a better chance to penetrate the entire internal pore structure.

2.9.2 Biochar dosage

Under constant HMs concentration and other conditions, the rate of HM adsorption will significantly increase as the biochar dosage increases. This effect is attributed to the increased active sites on the biochar which facilitate HM adsorption (Leng *et al.*, 2021). Normally, there is a direct positive correlation between biochar dosage and adsorption capacity or removal efficiency until saturation point is reached (Leng *et al.*, 2021). High biochar dosage enhances the adsorption of HMs due to abundant surface functional groups. However, the competition for the surface-active sites by HMs would gradually cause a reduction in the adsorption capacity of the biochar.

2.9.3 Pyrolysis Temperature

The pyrolysis temperature influences the chemical and physical characteristics of biochar, thus affecting the adsorption efficiency of HMs in wastewater (J. Li *et al.*, 2020). An increase in temperature to some certain extent improves the adsorption capacity of biochar by improving its porous structure. Further increase in temperature damages the structure, thus decreasing the porosity and surface area which lowers the adsorption performance.

2.9.4 Solution pH

The pH of the solution affects the surface property (charge) of biochar and the adsorption process by governing the speciation forms of heavy metal ions present in the solution (Chen *et al.*, 2015). At high pH, there is a stronger attraction between biochar and HMs due to increased negative charges on the surface of biochar which increases the adsorption of HMs. Even though the increase in pH increases negative charges, the majority of HMs turn to react with hydroxides (OH^-) and appear in the form of $\text{M}(\text{OH})_n$, $\text{M}(\text{OH})_{n-1}^+$, $\text{M}(\text{OH})_{n+1}^-$.

2.9.5 Contact time

Contact time is one of the important parameters during HMs adsorption on the surface of biochar. The adsorption efficiency of HMs on biochar is sharper at an initial stage and gradually becomes slow until equilibrium is reached as contact time increases (Wang *et al.*, 2021). Initially, high concentration triggers a quick diffusion of HMs ions from the solution into sufficient adsorption surface sites of biochar. Prolonged contact time leads to a decrease in adsorption sites and causes a slow adsorption process and saturation adsorption.

2.9.6 Coexisting ions

In addition to HM ions, natural or wastewater contains coexisting ions that influence the heavy metal adsorption process. The availability of SO_4^{2-} , Mg^{2+} , Na^+ , K^+ , and Ca^{2+} can decrease the HM ions removal capacity of biochar. The quantity of HM ions adsorbed reduces as ionic concentration decreases. This is due to intrinsic ions in the solution which are in competition with the HM cation for attachment on the surface of the biochar (Aigbe and Osibote, 2021). These coexisting cations turn to fill in the adsorption sites of the biochar surface, influencing the adsorption efficiency of HM ions.

2.9.7 Heavy-metals ion initial concentration

The heavy metal adsorption process also relies on the initial concentration of HM ions. The adsorption of HM ions on the surface of the biochar becomes stronger when the initial concentration of HM ions is high (Zhang *et al.*, 2019). The reason behind this effect could be that a higher concentration of HM ions augments the driving force to overpower the mass transfer resistance between biochar and solution, this increases the probability of collision between HM ions and biochar surface.

2.10 Adsorption isotherms used in this study

Adsorption isotherms explain the relationship between adsorbate concentration and its magnitude of accumulation on the surface of the adsorbent at a constant temperature (Araújo *et al.*, 2018). Mechanisms of adsorption can either be physical adsorption which relates to the van der Waals force formation, or chemical adsorption of the chemical bond formation and ion exchange (Wang and Guo, 2020).

2.10.1 Principles of adsorption isotherms used in this study

Langmuir model assumes that the adsorbent surface has an equal active adsorption site, monolayer surface coverage forms in the absence of interaction between molecules, and the surface is energetically homogenous (Xiong *et al.*, 2010). The Freundlich model estimates an increase in the concentration of ions on the adsorbent surface when there is an increase in the concentration of ions in the ambient solution and the model is valid for heterogeneous surfaces (Vassileva *et al.*, 2016). The Temkin adsorption isotherm assumes a linear decrease rather than a logarithmic decrease with coverage of heat of adsorption of entire molecules in the layer (Dada, 2012). Dubinin Radushkevich's adsorption isotherm suggests that the adsorption process occurs through the attachment of ions into the micropores of the adsorbent as opposed to layer-by-layer adsorption within pore walls (Inglezakis, 2007).

CHAPTER 3

MATERIALS AND METHODS

3.1 Sources of phytoremediation and non-phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*

Three phytoremediation biomasses of *C. citratus*, *C. nardus*, and *C. zizanioides* were obtained by growing these grasses in the mine tailings of the Bamagwato Concessions Limited (BCL) Cu-Ni mine (Figure 3.1). Non- phytoremediation biomasses were produced from non-contaminated soil collected around the vicinity of the BIUST experiment station. According to Magwaneng *et al.* (2017), BCL mine tailing consists of metal sulfides i.e. pyrite, chalcopyrite, pentlandite, and pyrrhotite in the form of mud. The BCL mine tailings are highly acidic with high amounts of heavy metals such as Cu, Ni, Pb, Mn, Zn, and As with the following concentrations of 5311.62, 2025.22, 552.81, 1137.53, 220.27, and 154.31 mg/kg, respectively (Ultra, 2020). For phytoremediation biomass, plants were grown under greenhouse conditions for four months while the non-phytoremediation biomasses were grown in BIUST soil. The biomasses were harvested and taken into a laboratory for further treatment before pyrolysis. Samples were air-dried at room temperature (25 °C) for 72 hours and oven-dried overnight at 105 °C. Samples were ground using Philips's mixer grinder to obtain finer particles and then subjected to pyrolysis.

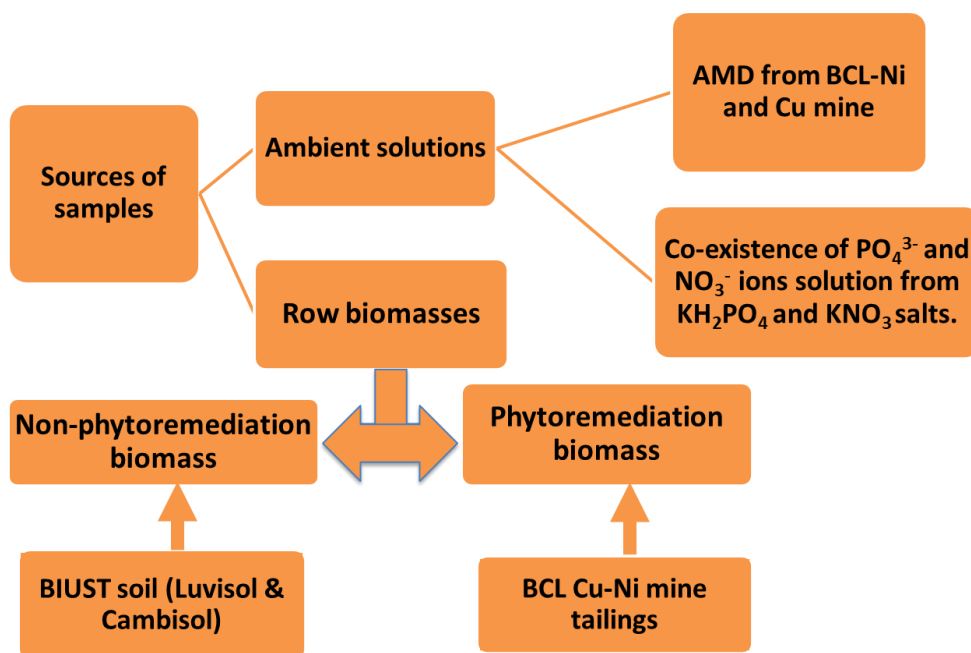


Figure 3.1. Sources of : non-phytoremediation and phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*, acid mine drainage, phosphate, and nitrate solutions.

3.2 Sources of acid mine drainage, phosphate, and nitrate solutions

Acid mine drainage samples were collected at five monitoring stations of the BCL Cu-Ni mine. Samples to be analyzed for cations (+) were preserved with 65% nitric acid (HNO₃) and transported to the laboratory at 4 °C to prevent oxidation reactions during transportation. The solution of the monitoring station with higher heavy metal concentrations was used in adsorption experiments. The phosphate and nitrate solutions were made from potassium dihydrogen phosphate and potassium nitrate salts, respectively.

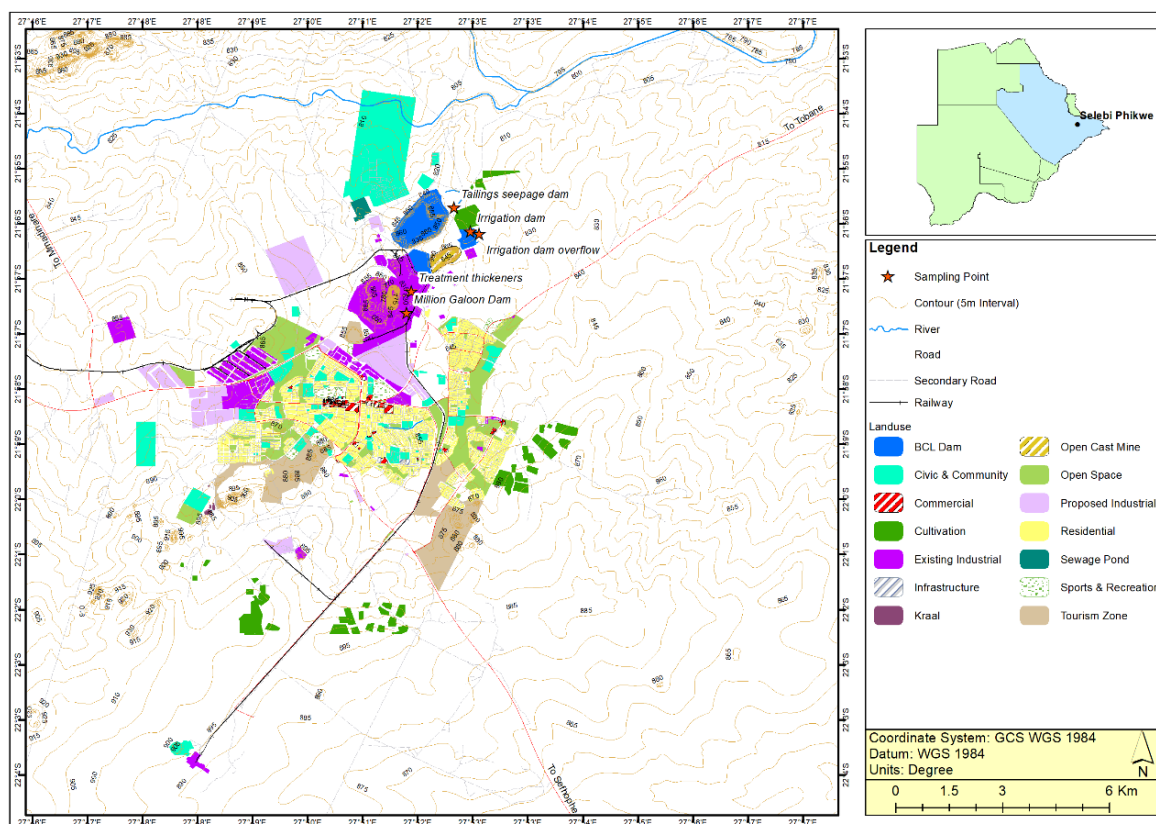


Figure 3.2. Acid mine drainage sampling sites.

3.3 Pyrolysis of phytoremediation and non-phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*

About 300 g of raw biomass for each batch was thermally heated in a 1-liter batch reactor at 550 °C in a nitrogen-flowing environment at residence time and heating rate of 30 minutes and 18°C/min, respectively. The condensable part of the product was condensed into a series of condensers: the first condenser (TK-02) was set at a temperature of 130°C, the second condenser (TK-03) was set at a temperature of 80°C and the third condenser (TK-04) was set to room temperature (25°C) to collect heavy oil, moderate oil, and pyrolysis liquids, respectively. For each raw material, three biochar preparations were performed.

The resultant biochar was packaged and sealed in polyvinyl-chloride (PVC) bags to be used in the next phase of the study. Percentage biochar yield was calculated using the following formula:

$$BC(\%) = \frac{BC}{R_{wi}} * 100 \quad (1)$$

Where: BC (%) is the biochar percentage yield,

R_{wi} is the weight of raw biomass,

And BC is the weight of biochar after pyrolysis.

3.4 Chemical characteristics of biomasses and biochars from phytoremediation and non-phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*

3.4.1 pH, EC, cations, heavy metals, ash content, volatile matter, and fixed carbon

The heavy metals concentrations (Fe, Cu, Ni, Al, and Mn) of raw biomasses and biochar samples were measured after acid digestion of 0.5g of biochar/raw biomass in a microwave digester (MA174 - Milestone Ethos Easy) at 200 °C for 2h using 2 ml of 30% hydrogen peroxide (H₂O₂) and 6 ml of concentrated nitric acid (HNO₃) followed by quantification using Inductively coupled plasma-optical emission spectrometry ((Thermo Scientific ICAP 7000 Series) ICP –OES).

The biochar pH and EC were measured in water suspension (1:20, biochar/water) after oscillation for 2h using a portable pH/EC meter.

The fixed carbon (FC), volatile matter (VM), and ash contents of biochar were determined by heating oven-dried biochar at 550 °C overnight in a muffle furnace for 5 hours, and the ash content, VM, and FC were calculated as follows (Saeed *et al.*, 2019):

$$\text{Ash Content (\%)} = \frac{W_2 - W_0}{W_1 - W_0} * 100 \quad (2)$$

$$\text{VM (\%)} = \frac{W_1 - W_2}{W_1} * 100 \quad (3)$$

$$\text{FC(\%)} = 100 - (\text{VM(\%)} + \text{Ash content(\%)}) \quad (4)$$

Where: W_0 = weight of empty crucible (g), W_1 = weight of crucible (g) + weight of biochar sample (g), W_2 = weight of crucible (g) + weight of mash sample after furnace heating (g).

3.4.2 Surface functional groups analysis

Pulverized samples of the raw biomasses, ordinary, and activated biochars were analyzed using FTIR spectroscopy (USA Nicolet IS5). The FTIR spectra were recorded at a wavelength range of 1000cm^{-1} to 4000 cm^{-1} and a resolution of 4 cm^{-1} . The infrared (IR) spectrum table was used to interpret the FTIR spectra (Chen *et al.*, 2021).

3.4.3 X-ray diffraction patterns analysis

The crystalline minerals composition of the pulverized samples of the raw biomasses, ordinary and activated biochars samples were analyzed using X-ray diffraction (Xrd) data derived from a Bruker D8 Advance powder diffractometer, a Cu tube X-ray source, and a LynxEye XE energy-dispersive strip detector. The instrument used a Cu- $K\alpha$ at a wavelength of 1.54056 and 2θ between 10 and 80 degrees and steps of 0.02 degrees at a rate of 0.500 sec/step . The machine was operated at 40mA and 40kV .

3.4.4 Scanning electron microscope (SEM) analysis

Ordinary and activated biochar samples were first coated with carbon and the density and shapes of the surface pores were characterized using a scanning electron

microscope at a working distance, voltage, and magnification of 10 mm, 15.0 kV, and x1700 μm , respectively.

3.5 Activation biochars from phytoremediation and non-phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*

Chemical activation of the phytoremediation and non-phytoremediation biochars was carried out using 0.1 M ZnCl_2 . Biochar and ZnCl_2 solution were mixed in a ratio of 10g:100mL (1:10; biochar to ZnCl_2). The mixing was performed at 25°C for 24 hours. After mixing, the slurry was dried in an oven at 105°C overnight. The solid-activated biochar was then washed with distilled water several times. The resulting biochar was dried at 110°C for 24 hours (Abd-Rahman *et al.*, 2019).

3.6 Point of zero charge analysis of ordinary and activated biochars from phytoremediation and non-phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*

The net charge of biochar samples was determined using a modified procedure from the study conducted by (Liu *et al.*, 2015). The pH of 0.01 M sodium chloride (NaCl) solution was adjusted between 2, 4, 6, 8, 10, and 12 using either 0.1 M hydrochloric acid (HCl) or 0.1 M sodium hydroxide (NaOH) solutions. At a selected pH, 20 ml of the aliquot of 0.01 M NaCl was mixed with 0.2g of biochar, and oscillating the mixture for 48 h. The change in pH ($\text{pH}_i\text{-pH}_f$) was plotted against the initial pH and the point of zero charge was determined where the graphs intercepted.

3.7 Chemical Characterization of the acid mine drainage solution

A 20 ml of AMD solution was filtered into 50 ml centrifuge tubes using 0.45 μm and the filtrate was analyzed for major and trace elements using Inductively coupled plasma-optical emission spectrometry (Thermo Scientific ICAP 7000 Series) ICP –OES. The anions were determined using Thermo Fisher DS 120 Ion Chromatography. The pH, EC, and TDS were analyzed by immersing an electrode probe of a multi-parameter instrument into 40 ml AMD solution, and readings were recorded once the value on the multi-parameter instrument stabilized.

Heavy metal concentration results of the 5 monitoring stations exhibit 1.27-13.23, 0.11-0.93, 2.46-109.5, 0.28-7.78, and 0.67-35.76 mg kg^{-1} ranges of Al, Cu, Fe, Ni, and Mn, respectively as shown in table 1.1. Drainage from the tailings dam has higher contents of Al, Cu, Fe, Ni, and Mn as compared to other monitoring stations of the mine. The solution pH of the 5 monitoring stations ranges between 2.29 and 6.77 with the lowest pH value (2.29) observed in seepage from the tailings. The effluent from the irrigation overflow dam has the lowest concentrations of heavy metals and a slightly acidic pH (6.77).

Table 3.1. Heavy metal contents and pH of acid mine drainage solution.

BCL-mine stations	monitoring	Al	Cu	Fe	Ni	Mn	pH
mg kg ⁻¹							
Million-gallon dam		4.48b	0.18a	14.53b	7.78a	1.32b	5.16b
Treatment thickeners		2.52b	0.21a	7.02c	2.51b	0.96b	6.54a
Tailings dam		13.23a	0.67a	109.5a	7.64a	35.76a	2.29c
Irrigation dam		4.90b	0.93a	6.27c	1.50b	0.67b	6.41a
Irrigation overflow dam		1.27b	0.11a	2.46d	0.28c	0.47b	6.77a
P-values as per monitoring stations		0.22ns	0.36ns	0.000***	0.000***	0.23ns	0.36ns

¹Means within the same column, followed by the same letter(s) are not significantly different according to Turkey's homogeneity test at 5% significance. *:significant, **:highly significant, ***:very highly significant; NS :non-significant.

3.8 Heavy metals adsorption by ordinary biochars, PO₄³⁻ and NO₃⁻ ions adsorption by ordinary and activated biochars from phytoremediation and non-phytoremediation biomasses

The adsorption experiments were conducted following a modified procedure of the study conducted by (Alagha *et al.*, 2020). Heavy metal concentrations in aliquot solution after adsorption experiments were analyzed using Thermo Scientific ICAP 7000 Series ICP – OES while PO₄³⁻ and NO₃⁻ concentrations were analyzed using Thermo Fisher DS 120 Ion Chromatography (IC).

3.8.1 Effect of biochar dosage on heavy metals adsorption by ordinary biochars, PO₄³⁻ and NO₃⁻ adsorption by ordinary and activated biochars from phytoremediation and non-phytoremediation biomasses

Effect of biochar dosage on Al, Cu, Fe, Ni, Mn, PO₄³⁻ and NO₃⁻ adsorption performance was carried in 40 ml of either AMD PO₄³⁻ and NO₃⁻ co-existing ions solution for 24h at an orbital speed of 180 rpm and biochar rates of 20mg/L, 100mg/L, 200mg/L,

1000mg/L, and 2000mg/L. The mixtures were filtered using a 0.45 μm filter and for heavy metal concentrations, filtrates were analyzed using Inductively coupled plasma-optical emission spectrometry (Thermo Scientific ICAP 7000 Series) ICP –OES while for PO_4^{3-} and NO_3^- , the equilibrium concentrations were analyzed using Thermo Fisher DS 120 Ion Chromatography.

3.8.2 Effect of pH on PO_4^{3-} and NO_3^- adsorption by ordinary and activated biochars from phytoremediation and non-phytoremediation biomasses

A biochar dosage of 0.04g of each sample was added into 40 ml of PO_4^{3-} and NO_3^- solution at an orbital speed of 180 rpm for 24h. The pH of the co-existence of PO_4^{3-} and NO_3^- solution was altered using either 0.1M HCL or 0.1M NaOH solutions to pH 2, 4, 6, 8, 10, and 12. The concentrations of PO_4^{3-} and NO_3^- aliquot solution were analyzed using Thermo Fisher DS 120 Ion Chromatography.

3.8.3 Effect of contact time on heavy metals adsorption by ordinary biochars, PO_4^{3-} and NO_3^- adsorption by ordinary and activated biochars from phytoremediation and non-phytoremediation biomasses

A biochar dosage of 0.04g of each sample was added into 40 ml of either PO_4^{3-} and NO_3^- or AMD solutions at an orbital speed of 180 rpm at a solution pH of 8. The mixture was oscillated for 0.3, 0.5, 1, 2, 4, and 8h. The mixtures were filtered using 0.45 μm and for heavy metal adsorption, filtrates were analyzed using Inductively coupled plasma-optical emission spectrometry (Thermo Scientific ICAP 7000 Series ICP –OES) while PO_4^{3-} and NO_3^- ,

the equilibrium concentrations were analyzed using Thermo Fisher DS 120 Ion Chromatography (IC).

3.8.4 Effect of initial concentration of PO_4^{3-} and NO_3^- in artificial wastewater and their adsorption by ordinary and activated biochars from phytoremediation and non-phytoremediation biomasses

A biochar dosage of 0.04g of each sample was added into 40 ml of PO_4^{3-} and NO_3^- solution at an orbital speed of 180 rpm for 1h at a solution pH of 8. The initial concentrations of the PO_4^{3-} and NO_3^- solutions were prepared from 20, 50, 100, 200, 300, and 500 mg/l. The concentrations of PO_4^{3-} and NO_3^- aliquot solution were analyzed using Thermo Fisher DS 120 Ion Chromatography.

3.9 Computation of adsorption capacities and percentage removal efficiencies

The adsorption capacities and percentage removal efficiencies were computed using the following equations (Mehdizadeh *et al.*, 2014);

$$Q_e = \frac{(C_i - C_e)V}{M} \quad (5)$$

Where, Q_e : equilibrium adsorption capacity (mg/g)

C_i : initial concentration (mg/l)

C_e : equilibrium concentration (mg/l)

V : volume of the solution (l)

M : mass of the adsorbate (g)

$$R (\%) = \frac{(C_i - C_e)}{C_i} * 100 \quad (6)$$

Where, $R (\%)$: percentage efficiency removal

C_i : Initial concentration (mg/l)

C_e : equilibrium concentration (mg/l)

3.10 Adsorption isotherms used in this study

To describe the equilibrium adsorption isotherms, the initial equilibrium data were fitted into seven (7) isotherm models, i.e. The Langmuir 1, 2, 3, and 4 models, The Freundlich model, The Temkin model, and The Dubinin Radushkevish model. The forms of the models are expressed in table 1 (Foo and Hameed, 2010; Itodo *et al.*, 2011).

From the Temkin equation, R and T represent the general gas constant ($\text{Jmol}^{-1} \text{K}^{-1}$) and T is the absolute temperature (K), b_T and A_T are the represents maximum adsorption capacity (mg g^{-1}), and adsorption isotherm constant which were computed from the slope and intercept of the linear plot of q_e vs $\ln C_e$. Ultimately, ϵ is the characteristic energy of adsorption (emissivity), K_{ad} and q_s are the Stephen Brunauer constant and maximum adsorption capacity from the slope and intercept of the linear plot of $\ln q_e$ vs ϵ^2 . The best fitting isotherm for PO_4^{3-} and NO_3^- adsorption was chosen based on the highest correlation factor closer to 1 as indicated in Table 4.17.

Table 3.2. Equilibrium adsorption isotherm models used in this study.

Isotherm	General Form	Linear Form	Eq.	Plot	Citation
Langmuir equation 1	$q_e = q_m K_a C_e / (1 + K_a C_e)$	$1/q_e = (1/K_a q_m) 1/C_e + 1/q_m$	(7)	$1/q_e$ vs $1/C_e$	(Majd <i>et al.</i> , 2022; Foo and Hameed, 2010)
Langmuir equation 2		$1/C_e = -K_L + q_m K_L 1/q_e$	(8)	$1/C_e$ vs $1/q_e$	
Langmuir equation 3		$1/q_e = q_m (1/K_a) (q_e/C_e)$	(9)	q_e vs q_e/C_e	
Langmuir equation 4		$Q_e/C_e = K_a q_m - K_a (q_e)$	(10)	Q_e/C_e vs q_e	
Freundlich	$q_e = K_F C_e^{1/n}$	$\log q_e = \log K_F + 1/n \log C_e$	(11)	$\log q_e$ vs $\log C_e$	
Temkin	$q_e = RT/b_T \ln A_T C_e$	$q_e = RT/b_T \ln A_T + (RT/b_T) \ln C_e$	(12)	q_e vs $\ln C_e$	
Dubinin Raduskevich	$q_e = (q_s) \exp(-K_{ad} \epsilon^2)$	$\ln(q_e) = \ln(q_s) - K_{ad} \epsilon^2$	(13)	$\ln(q_e)$ vs ϵ^2	

Where, q_e and C_e :are the equilibrium adsorption capacity (mg/g) and equilibrium concentration (mg L⁻¹) of the adsorbate, K_L and q_m represent Langmuir adsorption constant (L mg⁻¹) and q_m is the maximum adsorption capacity of the adsorbent (mg g⁻¹). K_a and q_m were computed from the intercept and slope of linear graphs of $1/q_e$ versus $1/C_e$ and $1/C_e$ versus $1/q_e$ for Langmuir models 1 and 2, respectively. The K_a and q_m from Langmuir 3 and 4 were calculated from linear plots of q_e vs q_e/C_e and q_e/C_e vs q_e , respectively. n from the Freundlich model represents the adsorption strength and K_F represents the maximum adsorption capacity (mg g⁻¹).

The separation factors were calculated and plotted for biochars that best fitted the Langmuir adsorption isotherm as depicted in figure 19. The separation factor R_L was calculated from the following equation:

$$RL = \frac{1}{1 + K_L C_o}$$

Where R_L is the separation dimensional factor, K_L refers to the Langmuir constant (L mg⁻¹) and C_o is the initial concentration of the adsorbate (mg l⁻¹). The separation factor explains the favorability of the adsorption, for $R_L > 1$, $R_L = 1$, and $0 < R_L < 1$, $R_L = 0$ the adsorption nature is unfavorable, linear, favorable, and irreversible, respectively (Foo and Hameed, 2010).

3.11 Statistical analysis of the data

The data were subjected to analysis of variance (ANOVA) for significant differences between 2 factors (grass types and biomass sources). When a significant difference exists, the mean comparison was performed using Turkey's homogeneity test at a 0.05 probability level. FTIR data with 55 peaks were subjected to principal component analysis (PCA) and the functional group with PCA loadings above ± 0.8 was considered the functional group contributing to the variability of samples. The biplots were generated to study the effects of heavy metals on the formation of surface functional groups. Pearson correlations were conducted between the chemical characteristics of raw biomasses and biochars and the principal component (PC) loadings.

Chapter 4

RESULTS AND DISCUSSION

4.1 Chemical compositions of phytoremediation and non-phytoremediation biomasses

This section describes the chemical composition of non-phytoremediation and phytoremediation biomasses used in the production of biochar. The non-phytoremediation biomass of *C. zizanioides*, *C. nardus*, and *C. citratus* was obtained by growing these grasses in non-contaminated soils collected from Palapye while the phytoremediation biomass was obtained from growing these plants in BCL mine tailings.

4.1.1 Elemental composition of phytoremediation and non-phytoremediation biomasses

The concentration of heavy metals in non-phytoremediation and phytoremediation raw biomass significantly differed from each other and between grass types (Table 4.1). Regardless of the grass types, the phytoremediation biomasses have higher heavy metal content (Al, Cu, Fe, Ni, and Mn) than the non-phytoremediation biomasses. In addition, the difference between phytoremediation and non-phytoremediation biomasses also differed between grass species. The Al concentration of non-phytoremediation biomasses ranged between 34.7 and 81.7 mg kg⁻¹ while phytoremediation biomasses had an Al concentration range of 166.23- 177.08 mg kg⁻¹ with no significant difference between grass species in the phytoremediation group.

Among non-phytoremediation biomasses, *C. nardus* had the highest Al content (81.7mg kg⁻¹) as compared to other grass species. *C. zizanioides* displayed the highest Cr concentration in both phytoremediation and non-phytoremediation biomasses. The Cu concentration of non-phytoremediation biomasses ranged from 0.75 mg kg⁻¹ to 1.23 mg kg⁻¹ with the highest Cu concentration observed in *C. zizanioides*. The phytoremediation biomasses displayed the Cu

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concentration range of 1.45-4.50 mg kg⁻¹ with a higher significant value observed in *C. nardus* (4.50 mg kg⁻¹) followed by *C. zizanioides* (2.41 mg kg⁻¹) and *C. citratus* (1.13 mg kg⁻¹), respectively. Among non-phytoremediation biomasses, Fe concentration was significantly higher in *C. nardus* (36.85 mg kg⁻¹) while *C. citratus* and *C. zizanioides* displayed almost similar Fe concentrations.

Table 4.1. Heavy metal contents of non-phytoremediation and phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*.

Grass type	Source of Biomass	Al	Cu	Fe	Ni	Mn
<i>C. zizanioides</i>	RV1	36.99c	0.75d	18.45c	0.17b	0.16b
<i>C. nardus</i>	RV2	166.23a	2.41b	142.52a	260.66a	0.19a
	RC1	81.7b	1.23cd	36.85b	2.28b	0.12c
<i>C. citratus</i>	RC2	177.08a	4.50a	20.00c	27.92b	0.25a
	RL1	34.7c	1.13cd	12.59c	2.83b	0.14a
	RL2	175.02a	1.45c	17.31c	4.67b	0.19a
P- values	TG	0.000***	0.000***	0.000***	0.000***	0.109ns
	SB	0.000***	0.000***	0.000***	0.000***	0.435ns
	TG *SB	0.002***	0.000***	0.000***	0.000***	ns

^aRV1: *C. zizanioides* non-phytoremediation RV2: *Chrysopogon zizanioides* phytoremediation, RC1: *Cymbopogon nardus* non-phytoremediation, RC2: *Cymbopogon nardus* phytoremediation, RL1: *Cymbopogon citratus* non-phytoremediation and RL2: *Cymbopogon citratus* phytoremediation.¹Means within the same column, followed by the same letter(s) are not significantly different according to Turkey's homogeneity test at 5% significance. *=significant, **=highly significant, ***= very highly significant; NS = non-significant.

In the phytoremediation group, *C. zizanioides* had a significantly higher Fe concentration compared to *C. zizanioides* and *C. citratus* which had comparable Fe

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concentrations. There was a significant interaction effect between the type of grass and source of biomass on Ni concentrations with *C. zizanioides* displaying significantly higher Ni concentration ($260.66 \text{ mg kg}^{-1}$) compared to other grass species. The concentration of Mn ranged between 0.12 and 9.25 mg kg^{-1} with the highest concentration (0.25 mg kg^{-1}) observed in *C. nardus* phytoremediation biomass.

Non-phytoremediation biomasses exhibited higher nutrient concentrations than phytoremediation biomasses with concentration ranges of 42.14-178.44, 524.24-1469.05, 358.01-404.83 and $151.82\text{-}208 \text{ mg kg}^{-1}$ corresponding to Na, K, Ca, and Mg, respectively (Table 4.2). Phytoremediation biomasses indicated concentration ranges of 12.86-17.34, 323.56-704.28, 279.39-306.46, and $91.15\text{-}166 \text{ mg kg}^{-1}$ for Na, K, Ca, and Mg kg^{-1} , respectively. According to the study conducted by Singh *et al.* (2016), heavy metals behaved similarly with essential cations as both consist of positive charges which compete for uptake by the root surface. Secondly, heavy metals inactivate the structure and function of functional proteins by reacting with sulfhydryl groups (-SH). Thirdly, heavy metals cause displacement of major cations (Na, K, Ca, and Mg) from specific binding sites which decreases their potential for uptake by plants, and therefore phytoremediation biomasses contain lower concentrations of essential nutrients.

Table 4.2. The concentrations of the essential nutrients of non-phytoremediation and phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*.

Grass type	Source of biomass	Na	K	Ca	Mg
<i>C. zizanioides</i>	RV1	42.14a	759.25b	358.01a	208a
	RV2	12.86a	704.28b	306.46a	166a
<i>C. nardus</i>	RC1	178.44a	534.24b	404.83a	151.82a
	RC2	17.34a	323.56b	284.17a	91.15b
<i>C. citratus</i>	RL1	46.5a	1469.05a	402.94a	162.45a
	RL2	14.2a	626.98b	279.39a	139.58a
P- values	TG	0.000***	0.000***	0.000***	0.000***
	SB	0.000***	0.000***	0.000***	0.000***
	TG *SB	0.002***	0.000***	0.000***	0.000***

^aRV1: *C. zizanioides* non-phytoremediation RV2: *Chrysopogon zizanioides* phytoremediation, RC1: *Cymbopogon nardus* non-phytoremediation, RC2: *Cymbopogon nardus* phytoremediation, RL1: *Cymbopogon citratus* non-phytoremediation, and RL2: *Cymbopogon citratus* phytoremediation.¹Means within the same column, followed by the same letter(s) are not significantly different according to Turkey's homogeneity test at 5% significance. *:significant, **:highly significant, ***: very highly significant; ns : non-significant.

These differences in the composition of exudates between plant species will contribute to the difference in the uptake of heavy metals amongst plant species (Chen *et al.*, 2022). The study by (Basant *et al.*, 2021), indicated that *C. zizanioides* had a bioaccumulation factor (BAF) of 0.80 for Ni and 0.24 for Cd while *C. citratus* had a BAF of 0.35 for Ni and 0.14 for Cd when grown in 4% Ni-Cd battery electrolyte waste-contaminated soil. Variation in heavy metals adsorbed by three phytoremediation plant species could be attributed to the difference in the heavy metal transport channels of these plant species.

Some of the heavy metal transporters include the Cation diffusion facilitator (CDF) family, heavy metal-transporting ATPases, natural resistance-associated macrophage protein (Nramp), metal transport proteins, and the Zinc-Tron permease (ZIP) family. Nramp transporters are responsible for the translocation of bivalent metals (Cd^{2+} , Fe^{2+} , Co^{2+} , Mn^{2+} , Cu^{2+}) from plants roots to shoots, metal transport proteins transport Ni and Zn. Heavy metal-transporting ATPases are responsible for the transportation of Pb, Co, Cd, and Zn in plants (Chukwuma *et al.*, 2020). These results confirmed that there exists variability in the heavy metal contents of the biomasses grown from contaminated and non-contaminated substrates and these variations are also dependent on the grass species. It is expected that variations in the chemical composition of the raw materials will be carried over into their respective biochar products.

4.1.2 Functional group profile of phytoremediation and non-phytoremediation biomasses

Surface group analysis data of raw biomass is shown in Figure 4.1. The peak at 1029 cm^{-1} was assigned to amine (C-N) stretching vibration such as epinephrine and dopamine while a small transmittance band at 1164 cm^{-1} was attributed to stretching vibration of the C-O bond in tertiary alcohol such as α -terpineol (Figure 4.1). The transmittance band at 1230 cm^{-1} belonged to the amine (C-N) functional group with a high intensity of the band observed in *C. nardus* amongst grass species. In comparison, the intensity of this peak slightly increased from non-phytoremediation biomass to phytoremediation biomass except for *C. nardus*. This suggests that heavy metals present in phytoremediation biomasses induced the amine functional group of the raw biomasses except for *C. nardus*. A small transmittance band at 1373 cm^{-1} may be assigned to C-H bending modes and the 1512 cm^{-1} bands were assigned to the stretching modes of nitro compound functional groups. The peak at 1585 cm^{-1} was assigned to C=C

stretching vibration caused by the aromatic structure and the band at 1737 cm^{-1} may be due to C=O stretching modes of carbonyl groups of carboxylic acids and esters such as lactones. The stretching vibration of the thiocyanate ($\text{S-C}\equiv\text{N}$) functional group of lignin was observed at 2166 cm^{-1} .

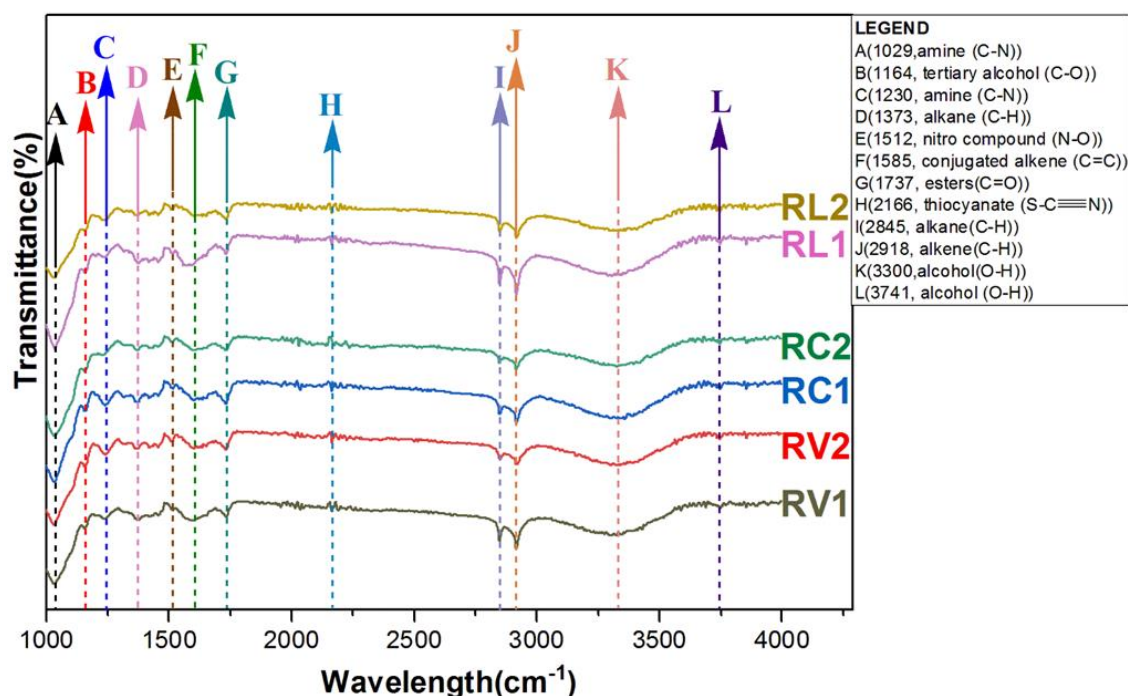


Figure 4.1. Surface functional groups of non-phytoremediation and phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*. RV1: *Chrysopogon zizanioides* non-phytoremediation biomass, RV2: *Chrysopogon zizanioides* phytoremediation biomass, RC1: *Cymbopogon nardus* non-phytoremediation biomass, RC2: *Cymbopogon nardus* phytoremediation biomass, RL1= *Cymbopogon citratus* non-phytoremediation biomass and RL2: *Cymbopogon citratus* phytoremediation biomass.

Sharp bands observed at 2845 and 2918 cm^{-1} were assigned to asymmetric and symmetric C-H stretching of methyl and methylene groups respectively or amine (N-H) stretching modes from primary amines. This agrees with the study conducted (Md, 2021), which found that bands at 2850 and 2918 cm^{-1} are attributed to the C-H stretching vibrations of methyl and methylene groups. The intensity of these functional groups among grass species descended as follows: *C.*

citratus>*C. zizanioides*>*C. nardus*. In comparison, the peak intensities of these two functional groups decreased from non-phytoremediation biomass to phytoremediation biomass. This could be attributed to the reduction in peak transmittance due to heavy metals load (Oves *et al.*, 2013).

4.1.3 X-ray diffraction patterns of phytoremediation and non-phytoremediation biomasses

Figure 4.2 shows the mineral composition of raw biomasses, amorphous carbon crystal phases (002) was observed at 2θ range of $20-30^\circ$ while talc (006) peaks formed at 2θ values of 28.8° and 40.8° in *C. zizanioides* non-phytoremediation and phytoremediation biomasses. As a function of height, *C. zizanioides*, non-phytoremediation, and phytoremediation biomasses had an intense talc peak as opposed to amorphous carbon peaks as indicated in table 4.8. According to Wang *et al.* (2022), the broadness of the peaks at 2θ range of $20-30^\circ$ is attributed to the presence of cellulose, hemicellulose, and lignin components.

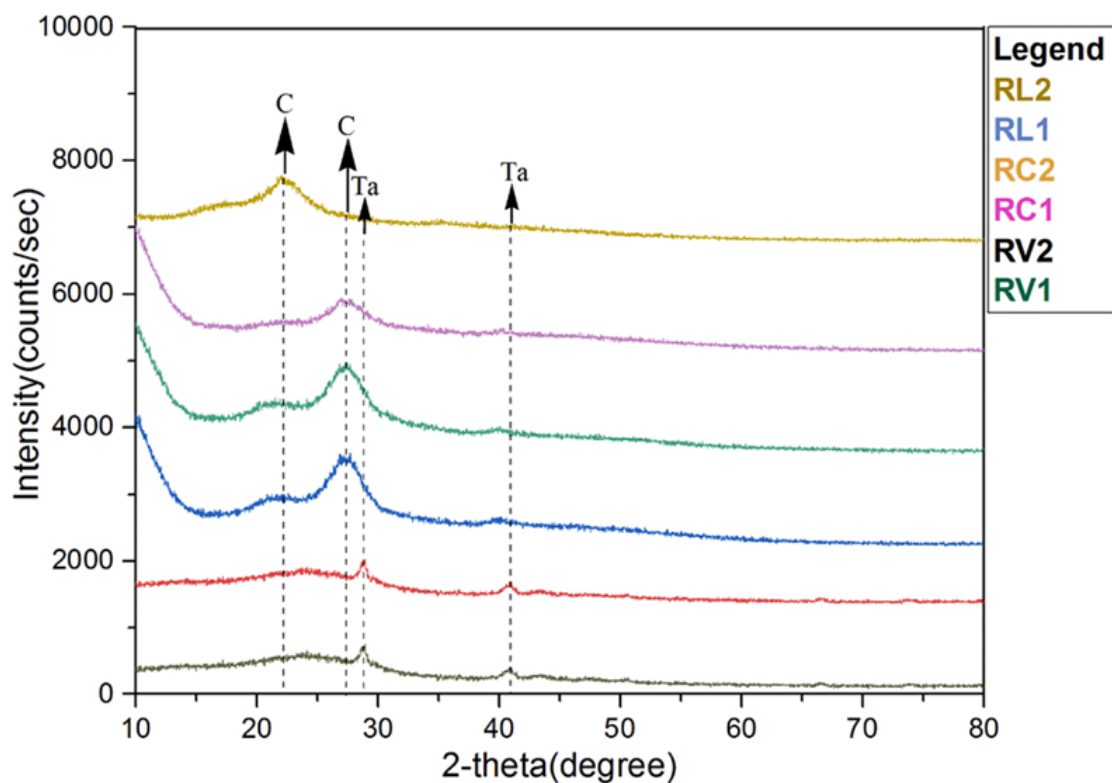


Figure 4.2. Crystalline minerals composition of non-phytoremediation and phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*. RV1:*Chrysopogon zizanioides* non-phytoremediation biomass, RV2:*Chrysopogon zizanioides* phytoremediation biomass, RC1:*Cymbopogon nardus* non-phytoremediation biomass, RC2:*Cymbopogon nardus*, phytoremediation biomass, RL1:*Cymbopogon citratus* non-phytoremediation biomass and RL2:*Cymbopogon citratus* phytoremediation biomass. C:amorphous carbon, Ta:talc.

4.2 Pyrolysis products and chemical compositions of biochars from phytoremediation and non-phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*

This section describes the pyrolysis products and the chemical composition of biochars derived from phytoremediation and non-phytoremediation biomasses.

4.2.1 Pyrolysis products

4.2.1.1 Percentage biochar yield

The biochar percentage yield of non-phytoremediation biomass ranged from 30.56 to 32.29% with the highest biochar yield value observed in *C. citratus* followed by *C. zizanioides* (31.94%) and *C. nardus*, respectively (Table 4.3). The difference in biochar yields from non-phytoremediation biomasses could be ascribed to the difference in cellular components of each species (Liu, *et al*, 2014). The percentage yield of biochars from phytoremediation biomasses ranged from 31.11 to 37.53% which was higher than those biochars from non-phytoremediation biomasses except for *C. zizanioides*.

Among the phytoremediation group, the biochar yield percentage was highest in *C. citratus* followed by *C. zizanioides* (31.76%) and *C. nardus*. The higher percentage biochar yield of biochars from phytoremediation biomass could be attributed to heavy metals as they form part of non-volatile, incombustible (inorganic) constituents thus increasing the mass of the biochar. The highest percentage biochar yield of biochar from *C. citratus* phytoremediation biomass could be ascribed to high lignin content. According to Tomczyk *et al* (2020), high lignin content favors higher biochar production as opposed to cellulose, and hemicellulose contents. The higher molecular weight and hydrophobicity of the lignin component make its structure resistant to breakdown and volatilization (Chukwuma *et al.*, 2020).

Table 4.3. Pyrolysis products derived from the pyrolysis of non-phytoremediation and phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*.

Grass type	Source of biomass	Pyrolysis Products		
		BC (%)	Liquid (%)	Syngas (%)
<i>C. zizanioides</i>	BCL1	31.94b	32.41a	48.62a
	BCL2	31.76b	29.38a	44.23a
<i>C. nardus</i>	BCC1	30.56b	32.41a	43.84a
	BCC2	31.11b	29.38a	39.12a
<i>C. citratus</i>	BCV1	32.29b	30.00a	38.21a
	BCV2	37.53a	27.41a	41.56a
SB Averages	Non-phytoremediation	31.63b	31.67a	43.55a
	Phytoremediation	33.47a	28.72b	41.64b
P Values	TG	0.020***	0.11ns	0.45ns
	SB	0.000***	0.000***	0.000***
	TG*SB	0.020***	0.46ns	0.37ns

^aBCV1:*Chrysopogon zizanioides* non-phytoremediation biochar, BCV2:*Chrysopogon zizanioides* phytoremediation biochar, BCC1:*Cymbopogon nardus* non-phytoremediation biochar, BCC2:*Cymbopogon nardus* phytoremediation biochar, BCL1:*Cymbopogon citratus* non-phytoremediation biochar, BCL2:*Cymbopogon citratus* phytoremediation biochar. BC (%) :biochar percentage yield, EC:electrical conductivity, TG:grass type and SB:source of biomass, ns: non-significant.

4.2.1.2 Percentage liquid yield

The liquid yield was not significantly affected by the interaction between grass type and sources, only the main effect due to the source of the biomass was observed (Table 4.3). On average, the liquid yield of phytoremediation biomasses was significantly lower than the counterpart indicating that the presence of heavy metals in the raw biomass will decrease the liquid yield even at 550 °C pyrolysis temperature. Stimulation of the phenolic secondary metabolic synthesis pathway due to heavy metals stress of the raw biomass increases its lignin content in the secondary cell thereby increasing cell wall thickness (Liu, *et al.*, 2018). According to (Jung, *et al*, 2008), cellulose and hemicellulose pyrolysis produces more bio-oil compared to lignin hence the low pyrolysis liquid yield of this current study could be contributed to the high lignin content of the raw biomass stimulated by the presence heavy metals.

4.2.1.3 Percentage syngas yield

There was no significant interaction effect on syngas yield observed between the type of grass and the source of the biomass, except for the source of the biomass. The syngas yield from the pyrolysis of phytoremediation biomasses was lower compared to the counterpart except for *C. citratus*. The difference in the syngas yield between non-phytoremediation and phytoremediation biomass could be attributed to the high amount of biochar produced concerning the overall product components. At the working temperature of this study, biochar is more favored than syngas formation which usually occurs at a higher temperature above 1000 °C (Zeng *et al.*, 2019). Ideally, the effect of higher raw biomass heavy metal content on syngas production could be observed at high temperatures wherein the presence of heavy metals increases syngas production due to its catalytic effect during pyrolysis.

4.2.2 Components of biochars from phytoremediation and non-phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*

4.2.2.1 Ash content

The ash content of biochar was not significantly affected by the interaction between grass type and sources, only the main effect due to the source of the biomass was observed (Table 4.4). On average, the ash content of biochar from non-phytoremediation biomasses was about 15.95% ranging from 12.45% to 17.83 % while those from phytoremediation biomass was about 19.59 % with a percentage range of 17.50 -25.23%. The increase in ash content of biochar from phytoremediation biomasses could be attributed to higher heavy metals loads which contribute to an increase in incombustible compounds of the biomass after pyrolysis. Inorganic compounds

such as Mg, K, Ca, and P contribute to the ash content of plant biomasses (Domingues *et al.*, 2017).

Table 4.4. The components and the chemical composition of biochars produced from non-phytoremediation and phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*.

Grass type	Source of biomass	Ash (%)	FC (%)	Vm (%)	pH	EC (μS/cm)
<i>C. zizanioides</i>	BCL1	17.57a	71.00a	11.43a	10.8a	4440a
	BCL2	25.23a	60.97a	13.80a	10.2a	3200b
<i>C. nardus</i>	BCC1	12.45a	74.23a	13.32a	9.5a	1120c
	BCC2	17.50a	68.62a	13.88a	9.3a	960c
<i>C. citratus</i>	BCV1	17.83a	65.91a	16.26a	10.25a	1375c
	BCV2	21.09a	63.39a	15.52a	9.70a	1080c
SB Averages	Non-phytorem	17.63b	68.51a	13.86b	10.18a	2311a
	Phytorem	19.59a	66.20b	14.21a	9.73b	1746b
P Values	TG	0.18ns	0.070ns	0.55ns	0.28ns	0.000***
	SB	0.000***	0.000***	0.000***	0.000***	0.000***
	TG*SB	0.14ns	0.056ns	0.43ns	0.28ns	0.000***

^aPhytorem:phytoremediation, BCV1:*Chrysopogon zizanioides* non-phytoremediation biochar, BCV2:*Chrysopogon zizanioides* phytoremediation biochar, BCC1=*Cymbopogon nardus* non-phytoremediation biochar, BCC2:*Cymbopogon nardus* phytoremediation biochar, BCL1:*Cymbopogon citratus* non- phytoremediation biochar, BCL2:*Cymbopogon citratus* phytoremediation biochar. BC (%) :biochar percentage yield, EC:electrical conductivity, VM: volatile matter, and FC:fixed carbon.

4.2.2.2 Fixed carbon content

The fixed carbon content of biochar was not significantly affected by the interaction between grass type and sources, only the main effect due to the source of the biomass was observed. On average, the percentage of fixed carbon of biochars from phytoremediation biomasses was lower than that of biochars from non-phytoremediation biomasses. The high percentage of fixed carbon in biochar indicates that the matrix still contains some original organic plant residues (Tomczyk *et al.*, 2020). During pyrolysis, the lignin component volatilizes at low rates as compared to hemicellulose and cellulose contents which may result in high fixed carbon.

Ideally, the heavy metals induce lignin formation in plants and consequently increase the fixed carbon of biochar from the phytoremediation biomass (Wang *et al.*, 2020). This study showed the opposite, implying that high heavy metal content in this pyrolysis condition will decrease the FC formation during pyrolysis. The low FC content of biochar from phytoremediation biomass suggests that the presence of heavy metals in the raw biomass favors the high transformation rate of plant original organic compounds into the volatile matter.

4.2.2.3 Volatile matter content

There was no significant interaction between the type of grass and the source of biomass of volatile matter content but only the source of the biomass significantly influenced the percentage of volatile matter content. On average, the volatile content of biochars from phytoremediation biomasses was higher than the counterpart corresponding to 14.21%, and 13.86%, respectively. The cellulose, hemicellulose, and lignin contents of the raw biomass influence the rate of volatile matter loss in the plant. During pyrolysis, cellulose, and hemicellulose devolatilize rapidly while lignin devolatilizes at a slow rate (Liu *et al.*, 2021). The higher volatile matter of biochar from phytoremediation biomass could be attributed to the catalytic effect of the heavy metals which promoted the decomposition of cellular components of the biomass (He *et al.*, 2019). Metals such as Zn, Cu, and Fe catalyze the decomposition of lignocellulose hence speeding up the devolatilization rate of cellular components of the grass biomasses (Liu *et al.*, 2021).

4.2.3 pH and EC of biochar derived from phytoremediation and non-phytoremediation biomasses

The interaction effect between the type of grass and source of biomass on biochar pH was insignificant. The pH of biochars derived from phytoremediation biomasses was slightly basic with an average pH value of 9.73 while the pH of biochar solutions of biochars from non-phytoremediation biomasses was more alkaline with an average pH value of 10.25. This suggests that hydrogen ions from heavy metals hydrolysis of biochar from phytoremediation biomasses could have contributed to the slight decrease in biochar pH. The alkaline pH of biochars from non-phytoremediation biomasses could be attributed to the released basic cations such as Mg^{2+} and Ca^{2+} during the thermal decomposition of raw biomasses (Rehrah *et al.*, 2014). Mineral nutrients such as Mg, Na, K, and Ca in ash exist in the form of carbonates or oxides which are alkaline after dissolution in water (Sun *et al.*, 2017). Oxygen-containing acidic functional groups add to the acidity of biochar, during pyrolysis the oxygen from O-containing acidic functional groups is lost increasing the pH of the biochar solution.

There was a significant interaction effect between the type of grass and the source of biomass on the electrical conductivity of biochar samples. Biochar from *C. zizanioides* indicated higher electrical conductivity for both non-phytoremediation (4440 $\mu S/cm$) and phytoremediation biomasses (3200 $\mu S/cm$) as compared to other grass species. The average EC of biochar from non-phytoremediation biomasses ranged from 1120 to 4440 $\mu S/cm$ while the EC of biochar from phytoremediation biomasses ranged from 960 to 3200 $\mu S/cm$ which was significantly lower than that of their counterparts. The difference in the EC values between grass types could be due to the difference in soluble salts assimilated into their structures during plant

growth (De Conto *et al.*, 2016). High electrical conductivity is positively correlated with high nutrient absorption by plants (Amari, *et al.*, 2017).

The low EC values of biochars from phytoremediation biomasses could be ascribed to nutrient deficiency due to competition between heavy metals and plant nutrients for absorption and translocation (Lu *et al.*, 2016). Heavy metals speciation forms in biochar can be divided into four fractions: residual fractions, exchangeable fractions, reducible fractions, and oxidizable fractions. Reducible fractions include hydrous oxides, Mn, and Fe oxides. Metal oxides formed in the biochar matrix of phytoremediation biochars could have contributed to low biochar EC due to fewer ions in an aqueous solution to conduct electrical currents.

4.2.4 Heavy metals and essential nutrients contents of biochars from phytoremediation and non-phytoremediation biomasses

Biochars displayed higher Al, Cu, Fe, Ni, Mn, Na, K, Ca, and Mg concentrations compared to their respective raw biomasses (Table 4.5 and Table 4.6). The K, Ca, and Mg concentrations of biochars from non-phytoremediation biomasses were higher than those of the counterpart (Table 4.6). Non-phytoremediation biochars indicated average concentration values of 1206.13, 466.31, and 187.76 mg kg⁻¹ corresponding to K, Ca, and Mg while phytoremediation biochars had K, Ca, and Mg average concentrations of 722.40, 348.01 and 144.10 mg kg⁻¹, respectively. A similar trend with that of the raw biomasses was observed for biochar samples indicating higher heavy metal contents of biochars from phytoremediation biomasses compared to biochars derived from non-phytoremediation biomasses regardless of the grass species. Specifically, biochar from *C. nardus* phytoremediation biomass displayed significantly higher Al concentration (470.69 mg kg⁻¹) compared other grass species which was 62% higher than the

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Table 4.5. The average heavy metal concentrations of biochars from non-phytoremediation and phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*¹.

Grass type	Source of biomass ^a	Al	Cu	Fe	Ni	Mn
mg kg ⁻¹						
<i>C. zizanioides</i>	BCV1	87.07d	2.27c	22.44d	3.83c	0.24b
	BCV2	183.78c	23.27a	170.92a	285.24a	0.28a
<i>C. nardus</i>	BCC1	323.10b	6.91b	38.75c	4.01c	0.37a
	BCC2	470.69a	8.99b	72.11b	25.61b	0.18c
<i>C. citratus</i>	BCL1	44.65e	2.60c	31.82cd	5.55c	0.21b
	BCL2	188.78c	3.20c	27.49d	8.82c	0.28a
SB average	Non-phytorem	151.61b	3.93b	31.00b	4.46b	0.27b
	Phytorem	281.08a	11.82a	90.17a	106.56a	0.25a
P- values	TG	0.000***	0.000***	0.000***	0.000***	0.307ns
	SB	0.000***	0.000***	0.000***	0.000***	0.435ns
	TG * SB	0.002***	0.000***	0.000***	0.000***	ns

^aPhytorem:phytoremediation, BCV1: *Chrysopogon zizanioides* non-phytoremediation biomass, BCV2:*Chrysopogon zizanioides* phytoremediation biomass, BCC1: *Cymbopogon nardus* non-phytoremediation biomass, BCC2:*Cymbopogon nardus* phytoremediation biomass, BCL1: *Cymbopogon citratus* non-phytoremediation biomass, BCL2:*Cymbopogon citratus* phytoremediation biomass, TG:type of grass, SB:source of biomass, and TG*SB:interaction effect between type of grass and source of biomass, ns: non-significant.

corresponding raw biomass. Biochar from *C. zizanioides* phytoremediation biomass indicated significantly higher Cu (23.27 mg kg⁻¹) Fe (170.92 mg kg⁻¹) and Ni (285.66 mg kg⁻¹) and concentrations compared to other grass species which were 89.6%, 16.6%, and 8.6% higher than the corresponding raw biomasses, respectively.

There was no significant difference between the source of biomass and grass types on Mn concentrations. Biochar from *C. nardus* phytoremediation biomass displayed significantly higher Mn (0.37 mg kg⁻¹) concentration compared to *C. citratus* and *C. zizanioides* which was 48% higher than the corresponding raw biomass. These results corroborated with the study conducted by Wang *et al.*, (2019), who reported that at the temperature range of 300 to 700°C,

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heavy metals in biochars were retained to approximately within the range of 91.1-97.49% for Zn, Cu, Cr, Ni, and Mn in the biochars. The high content of these metals in biochar was attributed to differences in the volatilization rate between these metals and the organic components of the raw materials. Organic substances are volatilized more readily than heavy metals thus, the HMs are retained in the biochar (Liu, *et al.*, 2018). The high pyrolysis temperature causes excitement of electrons which results in the loss of chemical bonds between heavy metals and organic compounds, thus releasing the organic compounds through volatilization and consequently enriching the concentrations of heavy metals in the biochar matrix.

Table 4.6. The essential nutrient concentrations of biochars from non-phytoremediation and phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*¹.

Grass type	Source of biomass ^a	Na	K	Ca	Mg
				mg kg ⁻¹	
<i>C. zizanioides</i>	BCV1	14.28a	994.62a	429.61a	226.72a
	BCV2	46.77a	922.60a	367.76a	180.94a
<i>C. nardus</i>	BCC1	19.25a	699.85a	485.79a	165.48a
	BCC2	198.07a	423.86a	341.01a	99.35a
<i>C. citratus</i>	BCL1	15.76a	1924.46a	483.53a	177.07a
	BCL2	51.61a	821.35a	335.27a	152.14a
SB average	Non-phytorem	16.43b	1206.31a	466.31a	187.76a
	Phytorem	98.82a	722.40b	348.01b	144.14b
P- values	TG	0.18ns	0.35ns	0.33ns	0.08ns
	SB	0.02***	0.09ns	0.43ns	0.57ns
	TG * SB	ns	ns	ns	ns

^aPhytorem: phytoremediation, BCV1: *Chrysopogon zizanioides* non-phytoremediation biomass, BCV2: *Chrysopogon zizanioides* phytoremediation biomass, BCC1: *Cymbopogon nardus* non-phytoremediation biomass, BCC2: *Cymbopogon nardus* phytoremediation biomass, BCL1: *Cymbopogon citratus* non-phytoremediation biomass, BCL2: *Cymbopogon citratus* phytoremediation biomass, TG: type of grass, SB: source of biomass, and TG*SB: interaction effect between type of grass and source of biomass, ns: non-significant.

4.2.5 Relationship between pyrolysis products, biochar components, and heavy metals of phytoremediation and non-phytoremediation biomasses

Biochar yield had a moderate positive correlation with Al ($r=0.491$), ash ($r=0.513$), and volatile matter ($r=0.546$) content but displayed a strong positive correlation with Cu ($r=0.72$) as shown in Table 4.7. Liquid yield displayed a very weak inverse relationship ($r=0.13$) but had a moderate inverse relationship with Al ($r=-0.40$), Fe ($r=-0.42$), and Ni ($r=-0.45$). A strong negative correlation ($r=-0.64$) was observed between liquid yield and Cu (Syngas yield displayed a very weak positive relationship with Al ($r=0.13$), and Mn ($r=0.02$), Cu ($r=0.25$), Fe ($r=0.21$) and Ni ($r=0.22$). Ash content indicated a weak negative correlation with Mn ($r=-0.22$) Al ($r=0.13$), Fe ($r=0.21$), and Ni ($r=0.22$). Ash content had a weak positive correlation with Fe ($r=0.26$), Ni ($r=0.28$), Al ($r=0.29$), and Cu ($r=0.33$). Volatile matter content had a weak positive relationship with Fe ($r=0.26$), Ni ($r=0.27$), Al ($r=0.28$), Pb ($r=0.33$), and Cu ($r=0.36$). Volatile matter content displayed a weak negative correlation with Mn ($r=-0.19$). Fixed carbon content showed a weak inverse correlation with Al ($r=-0.28$), Cu ($r=-0.36$), Fe ($r=-0.26$), and Ni ($r=-0.27$) but indicated a weak positive correlation with Mn ($r=0.19$).

4.2.6 Relationship between biochar components, chemical properties, and inherent heavy metals

Biochar yield displayed a very weak negative correlation with Mn ($r=0.11$) but displayed a moderate negative correlation ($r=-0.52$) with Al as depicted in Table 4.8. Biochar yield displayed a strong association with Cu ($r=0.720$) and Ni ($r=0.774$). Biochar pH had a weak negative correlation with Ni ($r=-0.36$). Biochar pH had a moderate negative correlation with Fe ($r=-0.483$) and Cu ($r=-0.544$). A strong negative correlation was observed between biochar pH and Al ($r=-0.789$). Biochar electrical conductivity had a moderate inverse relationship with Ni

($r=-0.42$), Fe ($r=-0.501$), and Cu ($r=-0.511$). A moderate negative correlation was observed between biochar EC and Al ($r=-0.614$).

Table 4.7. Pearson's correlation coefficients between pyrolysis products, biochar components, and heavy metal concentration of the raw biomasses.

Pyrolysis products and biochar components	Heavy metals				
	Al	Cu	Fe	Ni	Mn
BC (%)	0.49*	0.72**	0.40	0.45	-0.02
Liquid (%)	-0.40	-0.64**	-0.42	-0.45	-0.01
Syngas (%)	0.13	0.25	0.21	0.22	0.02
Ash	0.29	0.33	0.26	0.28	-0.22
VM	0.28	0.36	0.26	0.27	-0.19
FC	-0.28	-0.36	-0.26	-0.27	0.19

BC:biochar, VM:volatile matter and FC:fixed carbon.

Ash content displayed a very weak inverse relationship with Mn ($r=0.06$) but indicated a moderate negative correlation with Al ($r=-0.55$). Ash content had a weak positive relationship with Cu (0.33) but displayed a moderate positive association with Fe ($r=0.45$) and Ni ($r=0.50$). Volatile matter content displayed a very weak negative correlation with Mn ($r=-0.04$). A moderate negative correlation ($r=-0.50$) was observed between Al and volatile matter content. Cu had a weak positive association ($r=0.36$) with volatile matter content while Cu displayed a moderate positive association with volatile matter content. Fixed carbon content had a weak negative correlation with Cu ($r=-0.34$) but displayed a moderate inverse relationship with Fe ($r=-0.47$). Fixed carbon content displayed a moderate positive relationship with Al (0.53) and Ni ($r=0.52$).

Table 4.8. Pearson's correlation coefficient between biochar chemical properties and heavy metal contents of biochar.

Biochar chemical properties	Heavy metals				
	Al	Cu	Fe	Ni	Mn
BC (%)	0-.523*	0.720**	0.626**	0.774**	-0.11
pH	-0.789**	-0.544*	-0.483	-0.36	-0.551*
EC ($\mu\text{S}/\text{cm}$)	-0.614**	-0.511*	-0.501*	-0.42	-0.565*
Ash	-0.545*	0.33	0.45	0.502*	-0.06
VM	-0.534*	0.36	0.470*	0.519*	-0.04
FC	0.534	-0.36	-0.470*	-0.519*	0.04

BC:biochar, EC:electrical conductivity, VM:volatile matter and FC:fixed carbon.

4.2.7 Surface functional groups profile of biochars from non-phytoremediation and phytoremediation biomasses

There was a change in the functional group profile after the pyrolysis of non-phytoremediation and phytoremediation biomasses as shown in Figure 4.3. Pyrolysis temperature range of 350-650°C results in the breaking of chemical bonds of the biomass and the rearrangement of these bonds to form new functional groups (Tomczyk *et al.*, 2020). The broad transmittance band at 1075 cm^{-1} was assigned to the stretching mode of the C-O bond of primary alcohols such as methanol and propanol, the intensity of this functional group was higher in biochar from *C. nardus* phytoremediation biomass compared to the counterpart. Broad bands formed at 1411 and 1575 cm^{-1} were attributed to the aliphatic bending vibration of a methyl group (C-H) and the stretching vibration of cyclic alkene (C=C), respectively.

The intensity of the C=C functional group band was observed to be higher in biochar from *C. citratus* non-phytoremediation biomass compared to other grass species. A weak transmittance band formed at 1706 cm^{-1} was assigned to the stretching vibration of the C=O group of carboxylic acids such as 1-aminocyclopropane-1-carboxylic acid. Small peaks formed at 1992 cm^{-1} , 2171 cm^{-1} and 2202 cm^{-1} belonged to the stretching vibrations of allene (C=C=C), thiocyanate (S-C $\equiv$ C), and alkyne (C $\equiv$ C) functional groups, respectively. A weak transmittance

band at 3741 cm^{-1} belonged to the non-hydrogen bonded O-H functional group of alcohols; the band formation got enhanced across all samples after the pyrolysis of raw biomasses.

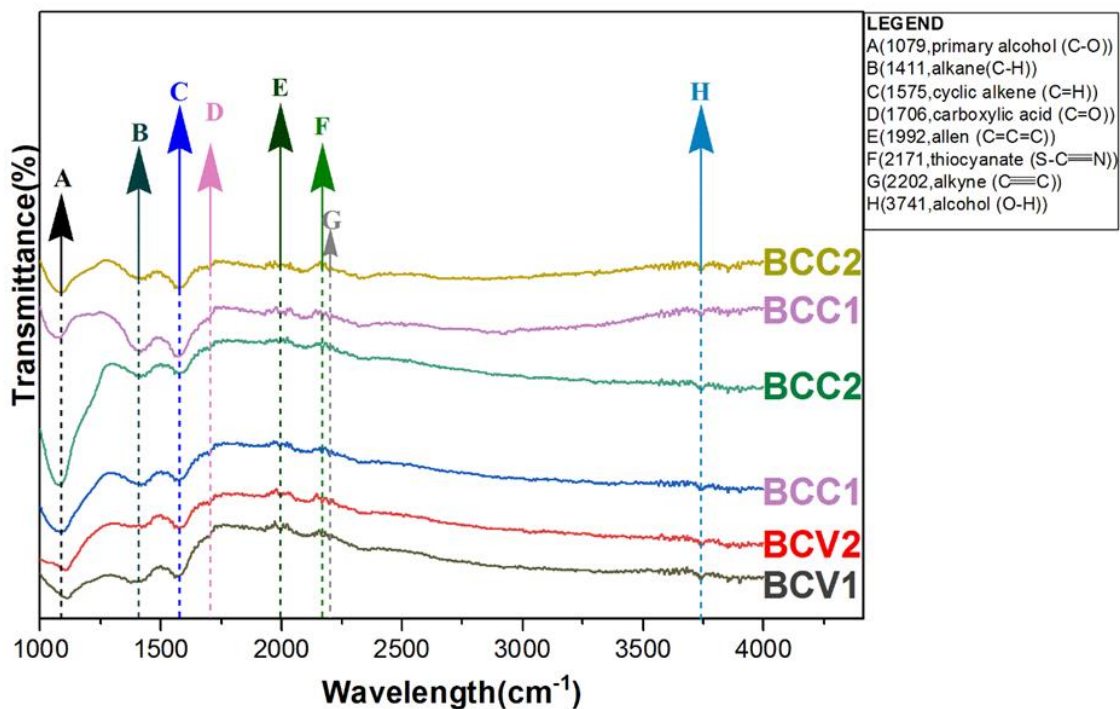


Figure 4.3. Surface functional groups of biochars derived from non-phytoremediation and phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*. BCV1:*Chrysopogon zizanioides* non-phytoremediation biochar, BCV2:*Chrysopogon zizanioides* phytoremediation biochar, BCC1:*Cymbopogon nardus* non-phytoremediation biochar, BCC2:*Cymbopogon nardus* phytoremediation biochar, BCL1:*Cymbopogon citratus* non-phytoremediation biochar, BCL2:*Cymbopogon citratus* phytoremediation biochar.

4.2.7.1 Relationship between biochar's functional groups and inherent heavy metals

FTIR data of biochars subjected to PCA resulted in the extraction of 2 PCs which contributed about 57.14% and 41.77% of data variance, corresponding to PC1 and PC2, respectively (Figure 4.4). PC1 was associated with primary alcohol, allene, thiocyanate, carboxylic acid, cyclic alkene, alkyne, and alkane while PC2 was associated with secondary alcohol. The biplot was able to discriminate biochar samples based on both types of grass species and the source of biomass. The biplot indicated an increase in the identified functional groups

from non-phytoremediation biochars to phytoremediation biochars for *C. nardus* and *C. zizanioides* while opposite effects occurred in *C. citratus*. Biochar from *C. nardus* and *C. citratus* phytoremediation biomasses had comparable values of a primary alcohol, allene, thiocyanate, carboxylic acid, cyclic alkene, alkyne and alkane, and alcohol functional groups.

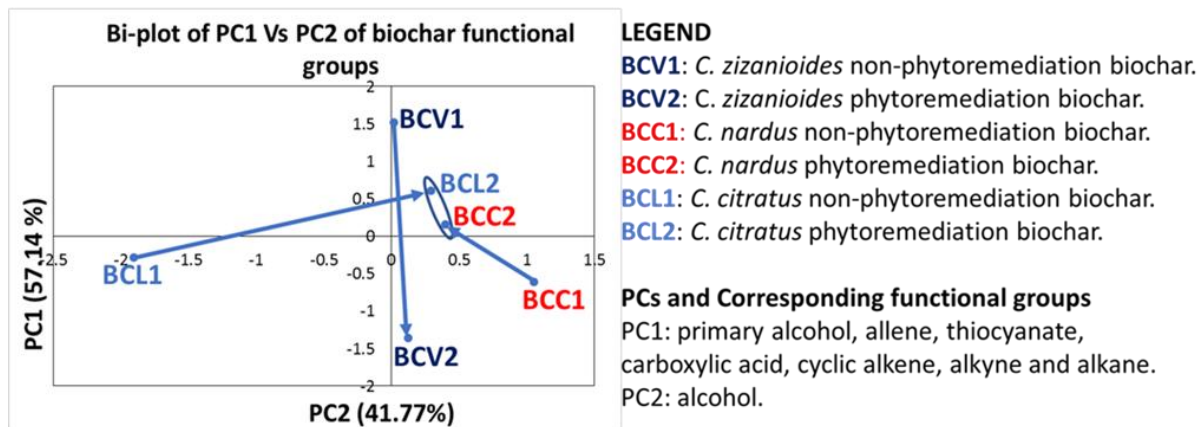


Figure 4.4 Biplot of PC1 vs PC2 of PCA extracted from surface functional groups of biochars derived from non-phytoremediation and phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*.

4.2.7.2 Relationship between biochar chemical properties and principal components (PCs)

PC1 had a very strong negative correlation with biochar pH and EC, and ash content but had a positive strong correlation with Al, Fe, and Ni while Mn had a positive moderate correlation with PC1 as indicated in Table 4.9. Fixed carbon content and volatile matter content displayed a strong positive correlation with PC1. PC2 displayed a very weak inverse relationship with Al, Cu, Fe, and Ni while biochar's EC had a very weak positive correlation with PC2. Mn, ash, and volatile matter contents displayed a weak negative relationship with PC2. Biochar pH and fixed carbon contents indicated a weak positive correlation with PC2.

Table 4.9. Pearson correlation coefficients between the scores of different principal components extracted from PCA of functional groups of biochar and chemical properties of biochars from non-phytoremediation and phytoremediation biomasses.

Factor	PC1	PC2
pH	-.872*	0.342
EC	-.827*	0.068
Ash	-0.791	-0.304
Vm	-0.796	-0.362
FC	0.796	0.362
Al	0.668	-0.185
Cu	0.34	-0.509
Fe	0.139	-0.72
Ni	0.075	-0.67
Mn	0.465	-0.385

EC:electrical conductivity, PC:principal component, EC:electrical conductivity, Vm:volatile matter and FC:fixed carbon

4.2.8 XRD patterns of biochars from non-phytoremediation and phytoremediation biomasses

The X-ray diffraction patterns of biochars from non-phytoremediation and phytoremediation biomasses are shown in Figure 4.5. New minerals such as antigorite (041), calcite (110), dolomite (021), geikielite (116), anatase (213), rutile (112), and corundum (119) were observed after pyrolysis of the raw biomasses. New peaks formed after pyrolysis of raw biomasses at 550°C indicate the enhancement of atomic order in the increasingly carbonized material indicating crystallization (Chatterjee *et al.*, 2020). The development of aromatic structures occurs after the complete fragmentation of the biomass during the pyrolysis process (Paris *et al.*, 2005). The decomposition of cellulose, hemicellulose, and lignin components during pyrolysis results in the volatilization of organic compounds increasing the concentration of mineral elements such as K, Mg, Ca, Si, and Na which participate in the formation of mineral compounds (Subratti *et al.*, 2021).

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Broad peaks indicating the presence of cellulose, hemicellulose, and lignin contents were observed at 2θ range of $20-30^\circ$. Sharp peaks of antigorite formed at 2θ value of 32.1° in *C. nardus* and *C. citratus* grass species. *C. citratus* non-phytoremediation and phytoremediation biochars had the sharp peaks of antigorite followed by *C. nardus* non-phytoremediation biochar while *C. nardus* phytoremediation biochars indicated a weak peak. A weak peak of calcite was observed in *C. zizanioides* phytoremediation biomass. Sharp dolomite peaks formed at 2θ value of 43.8° in *C. nardus* and *C. citratus* grass species. *C. citratus* non-phytoremediation and phytoremediation biochar had the sharp peaks of dolomite followed by *C. nardus* non-phytoremediation biochar while *C. nardus* phytoremediation biochars indicated a weak peak. The difference in the occurrence of mineral phases between grass species is attributed to their genotype variations, the genotype attributes affecting the mineral composition of grass or grass species involve their ability to: solubilize, uptake, translocate, bioaccumulate and utilize mineral elements (Clark, 1983).

Cymbopogon citratus non-phytoremediation and phytoremediation biochars were indicated to have almost equal anatase composition at 2θ value of 32.8° as the dominant mineral phase followed by dolomite, geikielite, rutile, corundum, amorphous carbon and anatase at 2θ value of 62.1° as indicated in Table 4.7. *C. nardus* non-phytoremediation biochar was dominated by anatase followed by amorphous carbon, dolomite, geikielite, and rutile while its corresponding phytoremediation form was dominated by anatase followed by amorphous carbon, dolomite, and geikielite, respectively. *C. zizanioides* non-phytoremediation biochar indicated the following descending order of mineral phases: talc (2θ value of 28.8°)>talc (2θ value of 40.8°)>calcite>amorphous carbon while phytoremediation biochar was dominated by

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talc at 2θ value of 28.8° followed by talc at 2θ value of 40.8° , carbon, and talc at 2θ value of 64.4° .

Weak peaks of geikielite were observed in *C. citratus* and *C. nardus* non-phytoremediation and phytoremediation biomasses at a 2θ value of 53.6° . Very small peaks of anatase were observed in *C. citratus* non-phytoremediation and phytoremediation biochars at a 2θ value of 62.1° . Another peak of talc formed at 2θ value of 66.4° in *C. zizanioides* non-phytoremediation biomass. A weak peak of rutile and corundum appeared at 2θ values of 69.8° and 77.1° , respectively in *C. citratus* non-phytoremediation and phytoremediation biomasses. The peak intensities of talc ($2\theta = 28.8^\circ$ and 40.8°), anatase ($2\theta = 32.8^\circ$) in *Chrysopogon zizanioides* and dolomite ($2\theta = 43.8^\circ$) in *Cymbopogon nardus* decreased from non-phytoremediation to phytoremediation biochars. According to (Han *et al.*, 2018), the weakening of peaks of phytoremediation biomasses is attributed to heavy metals as they inhibit the graphitization of the biochar and cause disordering of the carbon structures which results in lower activation energy.

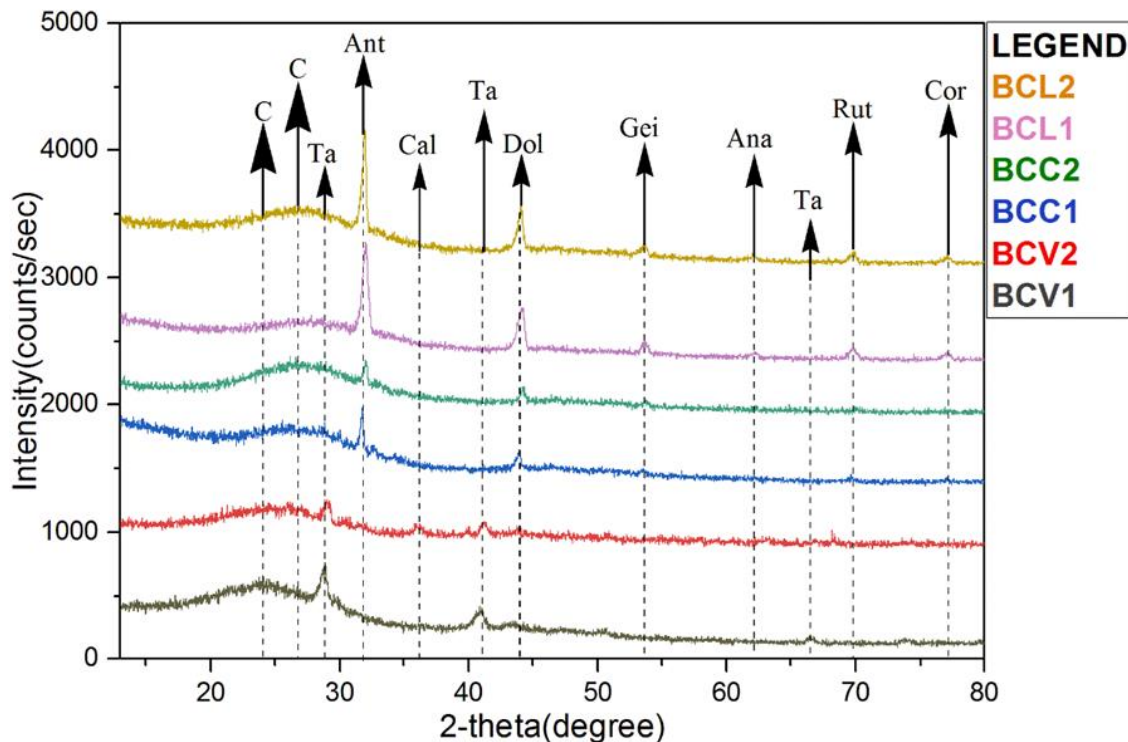


Figure 4.5. X-ray diffraction patterns of biochars from non-phytoremediation and phytoremediation biomasses based on the x-ray diffraction analysis. BCV1:*Chrysopogon zizanioides* non-phytoremediation biochar, BCV2:*Chrysopogon zizanioides* phytoremediation biochar, BCC1:*Cymbopogon nardus* non-phytoremediation biochar, BCC2:*Cymbopogon nardus* phytoremediation biochar, BCL1:*Cymbopogon citratus* non-phytoremediation biochar, BCL2:*Cymbopogon citratus* phytoremediation biochar. C: amorphous carbon, Ta: Talc, Ant: antigorite, Cal: calcite, Dol: dolomite, Gei: Geikielite, Ana: Anatase, Rut: Rutile, Cor: Corrondium.

4.2.9 Scanning electron microscope analysis of ordinary biochars from non-phytoremediation and phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*

Ordinary biochars from non-phytoremediation biomasses exhibited more porous surfaces as opposed to phytoremediation biochars as shown in Figure 4.6. According to (Liu *et al.*, 2017), the development of the pores in biochar samples is attributed to the decomposition of polymer chains of cellulose.

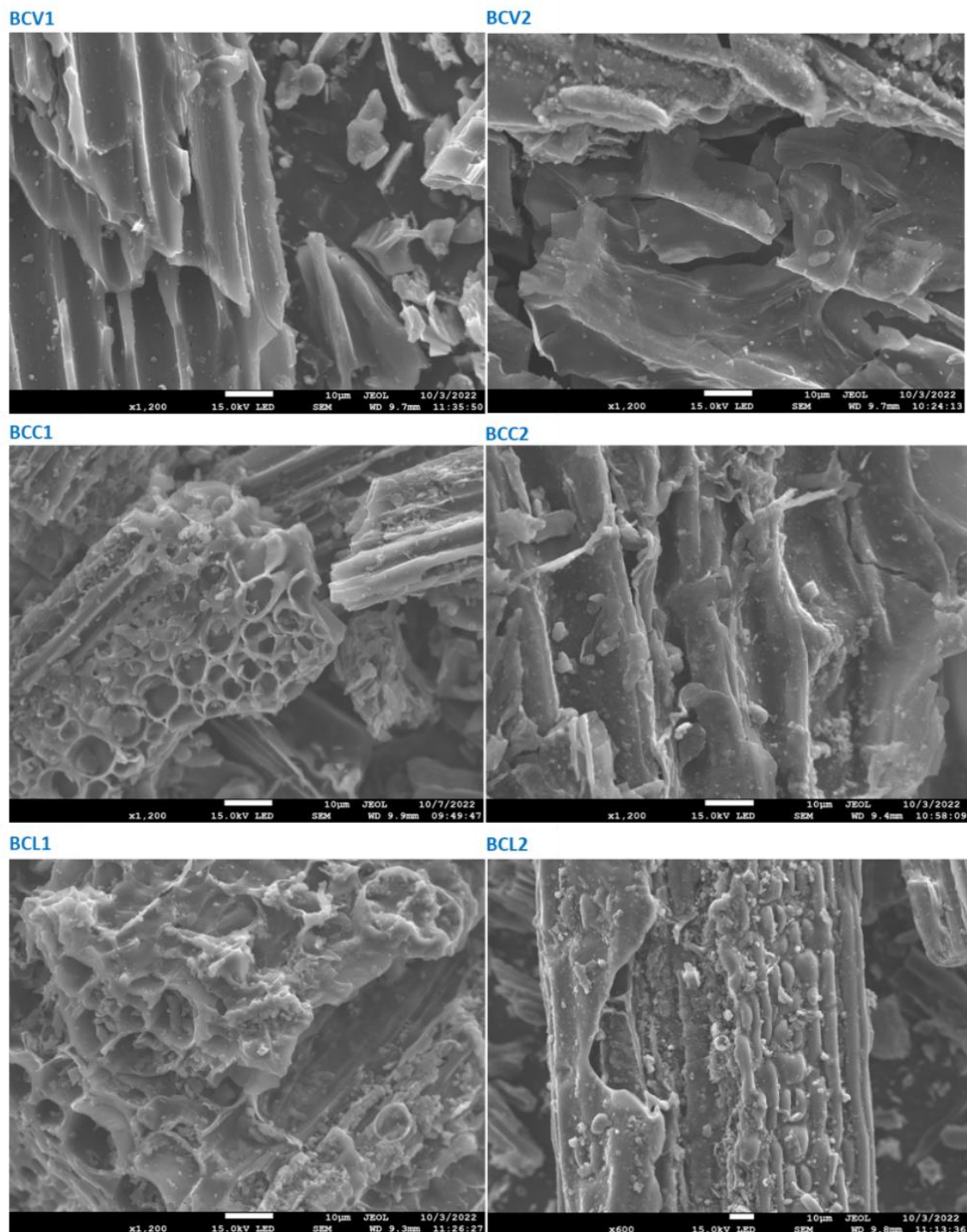


Figure 4.6. Surface morphologies of ordinary biochars from non-phytoremediation and phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*. BCV1:*Chrysopogon zizanioides* non-phytoremediation biochar, BCV2:*Chrysopogon zizanioides* phytoremediation biochar, BCC1:*Cymbopogon nardus* non-phytoremediation biochar, BCC2:*Cymbopogon nardus* phytoremediation biochar, BCL1:*Cymbopogon citratus* non-phytoremediation biochar, BCL2:*Cymbopogon citratus* phytoremediation biochar.

Amongst non-phytoremediation biomasses, biochar from *C. nardus* appears to have more micro-pores followed by *C. citratus* and *C. zizanioides* while *C. citratus* appears to have a more porous surface amongst phytoremediation biochars as opposed to other grass types. Few pores observed on the surfaces of phytoremediation biochars could suggest that biochar's impregnated heavy metals do not favor the formation of micropores within the biochar matrix. Most of the pores have surfaces that appear to be filled with small particles, (Nguyen *et al.*, 2022; Kumar *et al.*, 2018) attributed this observation to inorganic or minerals detected by XRD analysis.

4.3 Chemical compositions of activated biochars from non-phytoremediation and phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*

4.3.1 Surface functional groups analysis

ZnCl₂ activation did not alter the composition of the surface functional group profile of ordinary biochars as shown in Figure 4.7. The biplots of PC1 and PC2 of PCAs extracted from surface functional groups of both ordinary and activated biochars also indicated comparable percentages, PC1=57.10% and PC2=41.77% (ordinary biochars) and PC1=58.73% and PC2=39.95% (activated biochars) contributing to data variance. Similarly, the biplot of activated biochars (Figure 4.8) showed that surface functional groups got induced when *C. nardus* and *C. citratus* were grown in mine tailings while *C. zizanioides* behaved differently as indicated by arrows in Figure 4.7.

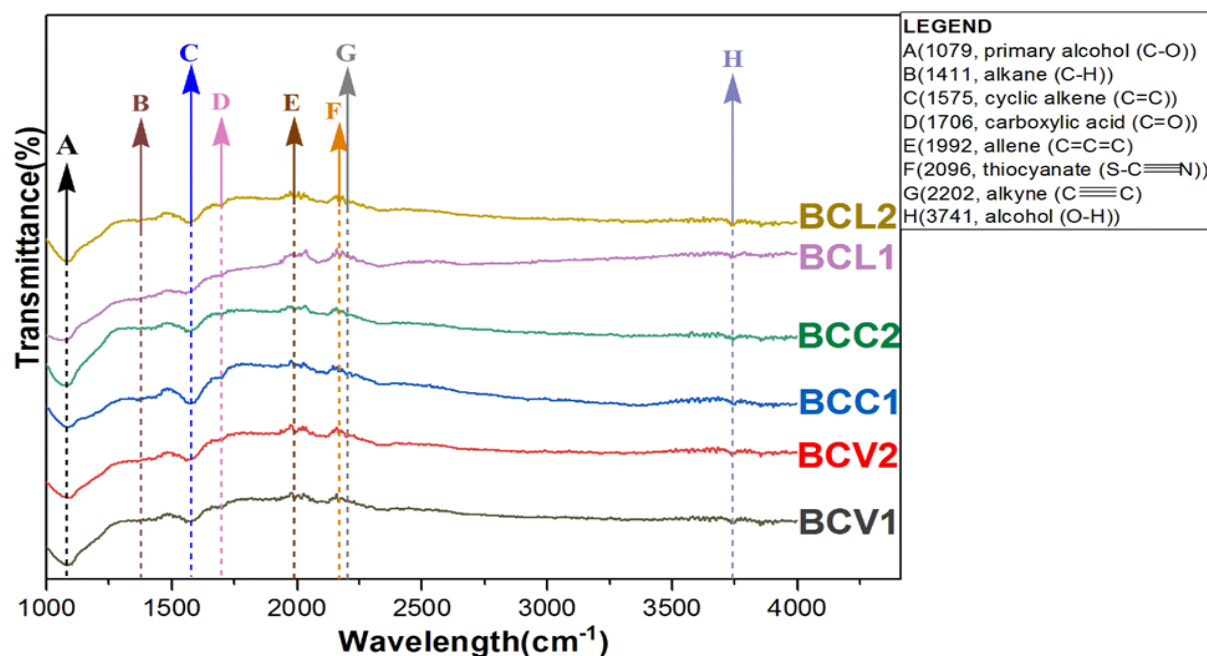


Figure 4.7. Surface functional groups of activated biochars derived from non-phytoremediation and phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*. BCV1:*Chrysopogon zizanioides* non-phytoremediation biochar, BCV2:*Chrysopogon zizanioides* phytoremediation biochar, BCC1:*Cymbopogon nardus* non-phytoremediation biochar, BCC2:*Cymbopogon nardus* phytoremediation biochar, BCL1:*Cymbopogon citratus* non-phytoremediation biochar, BCL2:*Cymbopogon citratus* phytoremediation biochar.

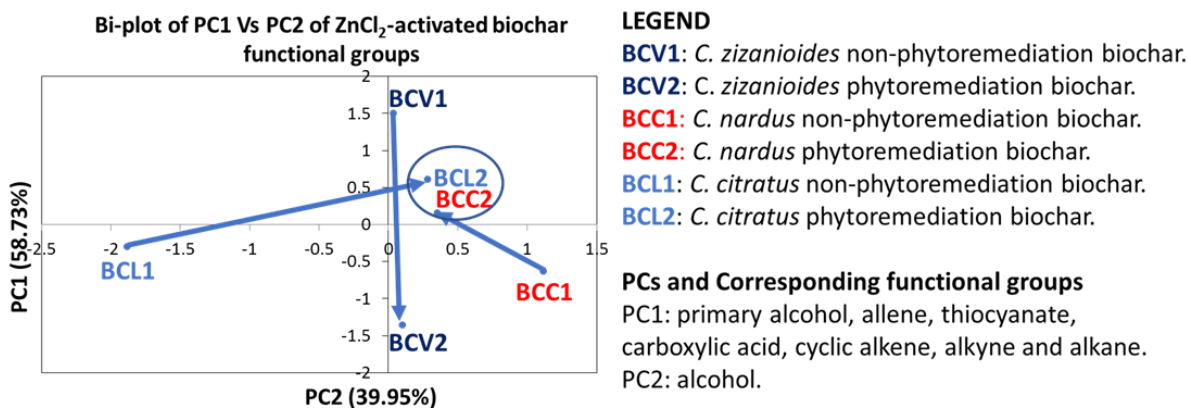


Figure 4.8. Bi-plot of PC1 vs PC2 of PCA extracted from ZnCl_2 -activated biochars from non-phytoremediation and phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*.

4.3.2 X-ray diffraction analysis

The activation process resulted in the broadening of amorphous carbon crystal phases, reduction in minerals phases, and introduction of new crystal minerals as depicted in Figure 4.9. This observation corroborates with the study conducted by (Syahida Arsyad *et al.*, 2021) as they found that broad peaks became stronger after activation using ZnCl_2 . Suresh *et al.* (2019), reported a change in mineral phase patterns of non-activated biochars due to activation using ZnCl_2 at 900°C but for this study, the change in diffractogram patterns occurred at 105°C . The formation of quartz (101), sphalerite (111), heulandite (-422), and chrysotile (008) after activation occurred at 2θ values of 26.6° , 27.2° , 28.1° , and 49.9° , respectively. Activated *C. citratus* non-phytoremediation biochar was dominated by amorphous carbon followed by heulandite and talc while the corresponding phytoremediation biochar was dominated by amorphous carbon only. Activated *C. nardus* was dominated by amorphous carbon followed by chrysotile while the corresponding phytoremediation biochar indicated the following descending order of mineral phases: quartz>heulandite>amorphous carbon>chrysotile. Heulandite was the dominate mineral in activated *C. zizanioides* non-phytoremediation biochar followed by amorphous carbon, talc at 2θ value of 28.8° which was almost equal to talc formed at 2θ value of 40.8° and lastly chrysotile. Activated *C. zizanioides* phytoremediation biochar was dominated by the heulandite mineral phase followed by amorphous carbon, talc, and quartz, respectively. The formation of sphalerite is attributed to the coordination of biochar's sulfonate functional group with residual Zn from ZnO (Terakado, *et al.*, 2021).

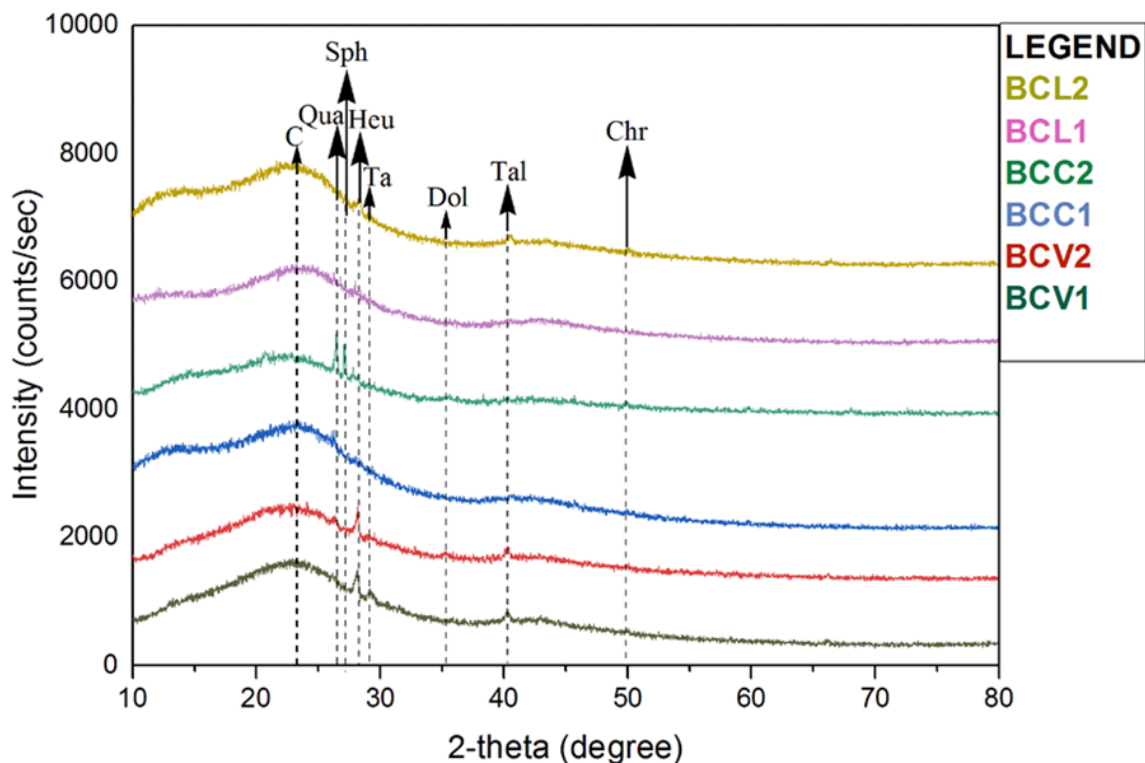


Figure 4.9. Minerals phases of ZnCl_2 -activated biochars from non-phytoremediation and phytoremediation biomasses detected based on the x-ray diffraction analysis. C: amorphous carbon, Qua:quartz, Sph: sphalerite, Heu:heulandite, Ta: talc, Dol: dolomite, and Chr:chrysotile. BCV1: *Chrysopogon zizanioides* non-phytoremediation biochar, BCV2: *Chrysopogon zizanioides* phytoremediation biochar, BCC1:*Cymbopogon nardus* non-phytoremediation biochar, BCC2:*Cymbopogon nardus* phytoremediation biochar, BCL1:*Cymbopogon citratus* non-phytoremediation biochar, BCL2: *Cymbopogon citratus* phytoremediation biochar.

Table 4.10. Summary of mineral phases detected in raw biomasses, ordinary and activated biochars based on the x-ray diffraction analysis.

Sample name	Form	Source	Dominant mineral phase
<i>Cymbopogon citratus</i>	Raw biomass	Non-phytorem	Carbon
		Phytoremediation	Carbon
	Ordinary biochar	Non-phytorem	Anatase($2\theta=62.1^\circ$)>Dolomite>Geikielite=Rutile>Corrondium>Carbon>Anatase ($2\theta=62.1^\circ$)
		Phytoremediation	Anatase($2\theta=62.1^\circ$)>Dolomite>Geikielite=Rutile>Corrondium>Carbon>Anatase ($2\theta=32.8^\circ$)
<i>Cymbopogon nardus</i>	Activated biochar	Non-phytorem	Carbon
		Phytoremediation	Carbon>Heulandite>Talc
	Raw biomass	Non-phytorem	Carbon
		Phytoremediation	Carbon
<i>Cymbopogon nardus</i>	Ordinary biochar	Non-phytorem	Anatase($2\theta=62.1^\circ$)>Dolomite>Carbon>Geikielite>Rutile
		Phytoremediation	Anatase>Carbon>Dolomite>Geikielite
	Activated biochar	Non-phytorem	Carbon>Chrysotile
		Phytoremediation	Quartz>Heulandite>Carbon>Chrysotile
<i>Chrysopogon zizanioides</i>	Raw biomass	Non-phytorem	Talc>Carbon
		Phytoremediation	Talc>Carbon
	Ordinary biochar	Non-phytorem	Talc($2\theta=28.8^\circ$)>Talc($2\theta=40.8^\circ$)>Calcite>Carbon
		Phytoremediation	Talc($2\theta=28.8^\circ$)>Talc($2\theta=40.8^\circ$)>Carbon>Talc($2\theta=66.4^\circ$)
	Activated biochar	Non-phytorem	Heulandite>Carbon>Talc ($2\theta=28.8^\circ$) =Talc ($2\theta=40.8^\circ$)>Chrysotile
		Phytoremediation	Heulandite>Carbon>Talc>Quartz

Phytorem:phytoremediation.

4.3.3 Scanning electron microscope analysis

SEM images of activated biochars from non-phytoremediation and phytoremediation biomasses are shown in Figure 4.10. Biochars indicate rough and undefined surfaces with cavities; some of the pores appear to be filled with small fragments just like ordinary biochars. Based on Figure 4.10, *C. citratus* non-phytoremediation biochar developed

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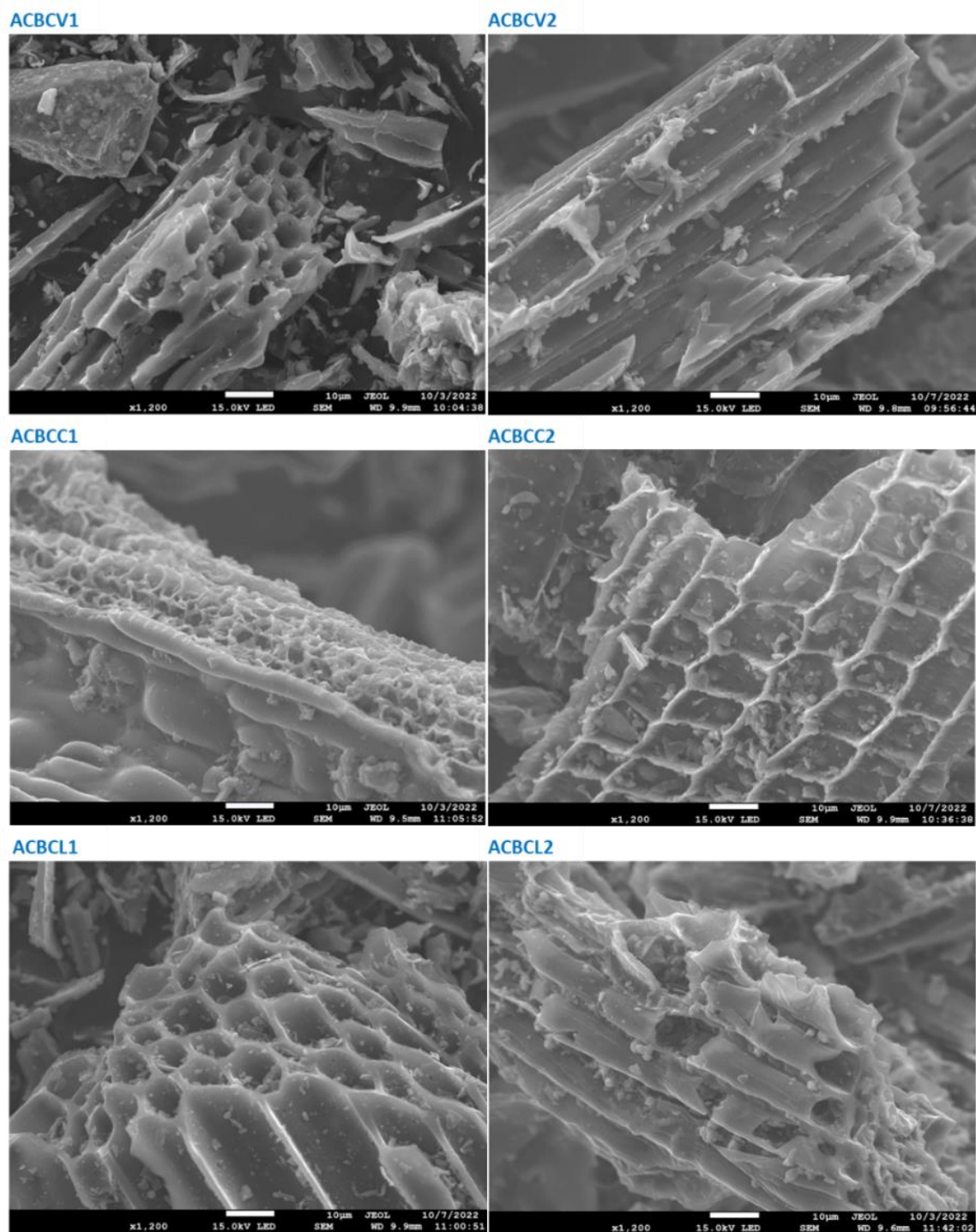


Figure 4.10. Surface morphologies of activated biochars from non-phytoremediation and phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*. AC:activated. ACBCV1:activated *Chrysopogon zizanioides* non-phytoremediation biochar, ACBCV2: activated *Chrysopogon zizanioides* phytoremediation biochar, ACBCC1:activated *Cymbopogon nardus* non-phytoremediation biochar, ACBCC2:activated *Cymbopogon nardus* phytoremediation biochar, ACBCL1:activated *Cymbopogon citratus* non-phytoremediation biochar, ACBCL2:activated *Cymbopogon citratus* phytoremediation biochar.

more micro-pores after activation followed by *C. citratus* and *C. zizanioides* non-phytoremediation biochars, and the same trend was observed in phytoremediation biochars. Activation using ZnCl_2 increased the surface porosity of biochar samples, this change is attributed to the overlapping and merging of several tiny pores (Ding *et al.*, 2021). According to the report by Machado *et al.* (2020), ZnCl_2 activation increases the inter- and intracell spaces by breaking downside bonds of cellulose molecules leading to the high porosity of biochar surfaces.

4.4 Point zero charge of ordinary and activated biochars from non-phytoremediation and phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*

If the pH of the solution is lower than the pzc value, it entails that the surface of biochar has a net positive charge but if the pH of the solution is greater than the pzc value it indicates that the surface is negatively charged (Al-degs *et al.*, 2008). Table 4.11 shows that the pH values of AMD, and the binary mixture of PO_4^{3-} and NO_3^- ions were lower than the pzc values indicating that biochar surfaces are positively charged hence they can be good potential adsorbents for anions. Ordinary biochars had pH_{pzc} values decreasing in the following order: $11.76 > 9.75 > 9.73 > 9.63 > 9.50$ corresponding to BCV1, BCV2, BCL1, BCC1, BCL1, and BCC2, respectively. Regarding the grass types, biochar from *Chrysopogon zizanioides* had a higher pzc value ($\text{pH}_{\text{pzc}}=11.76$) followed by *Cymbopogon citratus* ($\text{pH}_{\text{pzc}}=9.73$) and *Cymbopogon citratus* ($\text{pH}_{\text{pzc}}=9.72$) which had comparable values. The difference in the pH_{pzc} values between biochars produced from different grass types could be attributed to the difference in ash contents between biochars and their functional groups. According to the study conducted by Zhao *et al.* (2015), the net surface charge of biochar is affected by organic functional groups,

ash content, and present minerals. Banik *et al.*, (2018) attributed the positive charges on biochar surface to the pH-dependent oxonium and pyridium surface functional groups.

Table 4.11 indicates that regardless of the difference between grass species, heavy metals in biochars from phytoremediation biomasses lowered the pH at which biochars become neutrally charged. Zubir and Zaini (2020) reported that a decrease in pH_{pzc} is often attributed to increasing acidic functional groups on the biochar matrix. The pH_{pzc} values of the activated biochar samples descended in the following order: $6.38 > 6.28 > 6.25 > 6.00 > 5.75 > 5.49$, corresponding to BCV1, BCL1, BCL2, BCV2, BCC1, and BCC2, respectively. The degree of positive charges that may form and adsorb anions decreased after activating biochar samples with ZnCl_2 . This finding is attributed to the residual hydrogen ions in the biochar matrix following the activation procedure, which reduced the pH_{pzc} values of the ordinary biochars.

Table 4.11. Point zero charge of ordinary and ZnCl_2 -activated biochars from non-phytoremediation and phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*.

Sample code	Ordinary biochar		Activated biochar	
	pH	pH_{pzc}	pH	pH_{pzc}
BCV1	10.25	11.76	5.45	6.38
BCV2	9.70	9.75	5.09	6.00
BCC1	9.50	9.73	5.24	5.75
BCC2	9.30	9.50	5.06	5.49
BCL1	10.80	9.75	5.60	6.28
BCL2	10.20	9.63	5.11	6.25
PO_4^{3-} and NO_3^- solution	5.34			
AMD solution	2.29			

Pzc: point of zero charges, BCV1: *Chrysopogon zizanioides* non-phytoremediation biochar, BCV2: *Chrysopogon zizanioides* phytoremediation biochar, BCC1: *Cymbopogon nardus* non-phytoremediation biochar, BCC2: *Cymbopogon nardus* phytoremediation biochar, BCL1: *Cymbopogon citratus* non-phytoremediation biochar, BCL2: *Cymbopogon citratus* phytoremediation biochar.

4.5. Heavy metals, PO_4^{3-} and NO_3^- adsorption experiments

This section of the report is on the adsorption of heavy metals, phosphate, and nitrate ions by biochars from phytoremediation biomasses.

4.5.1 Effect of biochar dosage on heavy metals adsorption by ordinary biochars from non-phytoremediation and phytoremediation biomasses

Generally, negative adsorption capacities for Al, Cu, Fe, and Ni at biochar dosage of 0.0008g for most ordinary and activated biochars were observed and the magnitude of negative adsorption capacities was reduced with an increase in biochar dosages until the graph was constant at biochar dosage of 0.04 g as shown in Figure 4.11. It is suggested that adsorption of these heavy metals could not be favored due to repulsion forces between biochar inherent heavy metals and heavy metals present in acid mine drainage. The trend of the graphs from figure 4.11 mostly indicates that biochar samples had negative adsorption capacity values for Al, Cu Fe, and Ni at a biochar dosage of 0.0008g and the values started to increase with an increase in biochar dosage until equilibrium values were attained at 0.04g dosage. As per the literature review (Zhang *et al.*, 2019), when the pH of the solution is lower than the point of zero charges of the adsorbent, the adsorbent will be protonated causing electrostatic repulsion between adsorbent and positively charged adsorbate which results in the decrease of heavy metal adsorption by adsorbent surface.

The negative adsorption capacities and percentage removal efficiencies in Figure 4.11 and Table 4.12 could be attributed to the leaching of Al, Cu, Fe, and Ni into acid mine drainage which lowered the adsorption capacity values of biochar samples below zero. Activated *C. zizanioides* phytoremediation biochar had the maximum adsorption capacity of 5.33 mg g⁻¹ for Al which is 0.89 percent removal of the Al initial concentration as depicted in table 10. Ordinary *C. zizanioides* phytoremediation biochar showed the maximum adsorption capacity of 4.69 mg g⁻¹ for Ni as compared to other biochar samples. Mn adsorption capacities indicated a decreasing order; ACBCV2 (35.59 mg g⁻¹)> OBCC2 (31.83 mg g⁻¹) > OBCV2

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(20.33) > ACBCC2 (13.5 mg g⁻¹) > OBCL2 (5.83 mg g⁻¹) > ACBCL2 (-76.67 mg g⁻¹), respectively. It should be well noted that the diffusion of adsorbate onto the adsorbent surface does not only occur due to chemisorption but can also be accounted to physical sorption. (Shakoor *et al.*, 2020) explained that physical sorption entails the diffusion of heavy metals onto the pores of the biochar matrix.

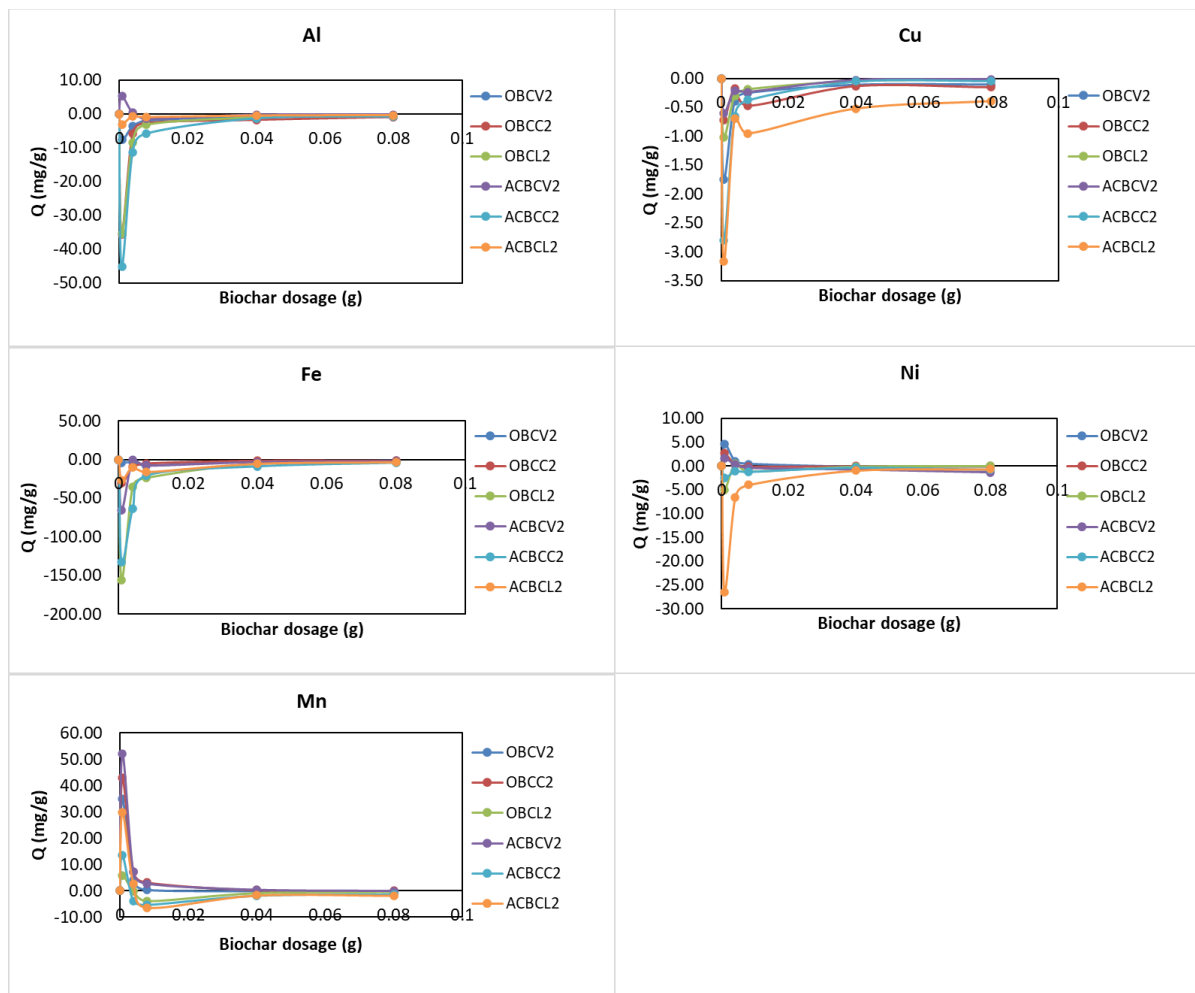


Figure 4.11. Effect biochar dosage on Al, Cu, Fe, Ni and Mn adsorption in acid mine drainage by drainage by ordinary biochars from phytoremediation and non-phytoremediation biomasses. OBCV2: ordinary *Chrysopogon zizanioides* phytoremediation biochar, BCC2: ordinary *Cymbopogon nardus* phytoremediation biochar, BCL2: ordinary *Cymbopogon citratus* phytoremediation biochar, ACBCV2: activated *Chrysopogon zizanioides* phytoremediation biochar, ACBCC2: activated *Cymbopogon nardus* phytoremediation biochar, ACBCL2: activated *Cymbopogon citratus* phytoremediation biochar.

4.5.2 Effect of contact time on Al, Cu, Fe, Ni, and Mn adsorption by ordinary biochars from non-phytoremediation and phytoremediation biomasses

Generally, ordinary and activated biochar samples did not adsorb Al, Cu Fe and Ni, and Mn when the mixtures were retained for 8hr as shown in figure 4.12. Most of the graphs did not show a uniform trend of adsorption capacities as a function of contact time. It was observed that most of the biochar samples reached equilibrium adsorption capacities after 4hr contact time. Ordinary biochars adsorbed Fe after 0.3hr and the sorption decreased until 1hr elapsed and increased until equilibrium adsorption capacities saturation point was reached after 4hr except for *C. zizanioides* biochar samples the results of this study do not corroborate with most of the literature due to the lack of uniformity of the graph trends. According to the study by Elaigwu *et al.* (2010) an observation was made that increasing contact time resulted in an increase in the removal efficiency of metal ions from AMD solution.

Table 4.13 indicates that activated *C. zizanioides* had the highest percentage removal of 7.38% for Al after 0.5hr contact time. Ordinary *C. zizanioides* showed negative adsorption capacity (-51.72 mg g^{-1}) for Cu implying that the sample released more Cu ions into acid mine drainage after 0.3hr contact time. Payus *et al.* (2014) conducted a study on a bone meal as an alternative for the treatment of AMD solution and they associated a uniform decreasing trend of Mg with its leaching into AMD solution. The highest percentage removal (14.56 %) of Fe was observed in activated *C. zizanioides* phytoremediation biochar after a contact time of 0.3h as compared to other biochar samples.

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Table 4.12. Effect of biochar dosage on heavy metals adsorption by biochars from non-phytoremediation and phytoremediation biomasses.

Sample code	Al			Cu			Fe			Ni			Mn		
	Qeh (mg/g)	Dosage at Qeh (g)	R (%)	Qeh (mg/g)	Dosage at Qeh (g)	R (%)	Qeh (mg/g)	Dosage at Qeh (g)	R (%)	Qeh (mg/g)	Dosage at Qeh (g)	R (%)	Qeh (mg/g)	Dosage at Qeh (g)	R (%)
OBCV2	-0.75	0.04	-11.28	-0.1	0.08	-35.8	-1.36	0.04	-2.76	4.67	0.0008	1.31	20.33	0.0008	1.21
OBCC2	-0.92	0.08	-15.37	-0.01	0.08	-23.05	-1.62	0.04	-1.65	2.63	0.0008	0.72	31.83	0.0008	1.89
OBCL2	-0.62	0.08	-9.39	-0.02	0.08	-0.03	-3.64	0.08	-7.4	2.47	0.0008	0.69	5.83	0.0008	0.35
ACBCV2	5.33	0.0008	0.89	-0.02	0.04	-5.8	-0.2	0.004	-0.2	1.12	0.04	1.52	35.59	0.0008	52.17
ACBCC2	-0.76	0.08	-12.64	-0.04	0.08	-14.02	-4.06	0.08	-8.24	-0.31	0.04	-4.39	13.5	0.0008	0.8
ACBCL2	-0.39	0.08	-6.54	-0.07	0.08	-21.26	-3.53	0.08	-7.18	-0.68	0.08	-18.39	-76.67	0.0008	-4.56

Qeh : highest equilibrium adsorption capacity and R (%) :percentage removal efficiency, OBCV2: ordinary *Chrysopogon zizanioides* phytoremediation biochar, BCC2: ordinary *Cymbopogon nardus* phytoremediation biochar, BCL2: ordinary *Cymbopogon citratus* phytoremediation biochar, ACBCV2: activated *Chrysopogon zizanioides* phytoremediation biochar, ACBCC2: activated *Cymbopogon nardus* phytoremediation biochar, ACBCL2: activated *Cymbopogon citratus* phytoremediation biochar.

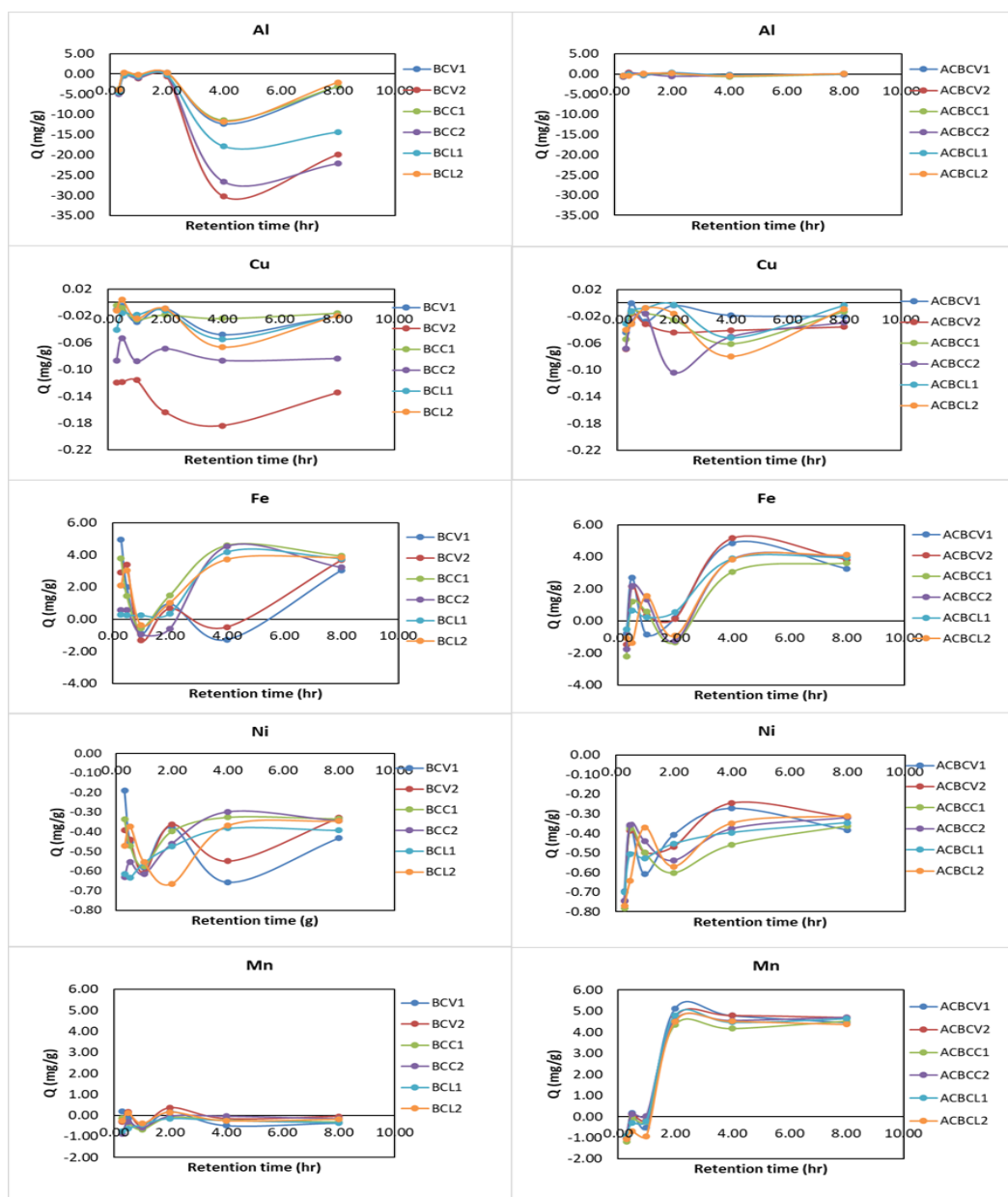


Figure 4.12. Effect of contact time on Al, Cu, Fe, Ni, and Mn sorption in acid mine drainage by drainage by ordinary biochars from phytoremediation and non-phytoremediation biomasses. BCV1: *Chrysopogon zizanioides* non-phytoremediation biochar, BCV2: *Chrysopogon zizanioides* phytoremediation biochar, BCC1: *Cymbopogon nardus* non-phytoremediation biochar, BCC2: *Cymbopogon nardus* phytoremediation biochar, BCL1: *Cymbopogon citratus* non-phytoremediation biochar, BCL2: *Cymbopogon citratus* phytoremediation biochar. ACBCV1: activated *Chrysopogon zizanioides* non-phytoremediation biochar, ACBCV2: activated *Chrysopogon zizanioides* phytoremediation biochar, ACBCC1: activated *Cymbopogon nardus* non-phytoremediation biochar, ACBCC2: activated *Cymbopogon nardus* phytoremediation biochar, ACBCL1: activated *Cymbopogon citratus* non-phytoremediation biochar, ACBCL2: activated *Cymbopogon citratus* phytoremediation biochar.

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Ni ion was observed to be leached highly in *C. citratus* as compared to other samples as it showed a negative percentage removal of 13.35. The highest percentage removal (4.33%) of Mn was achieved by activated *C. zizanioides* non-phytoremediation biochar as compared to other biochar samples. The report by Payus *et al.* (2014) further elucidates that heavy metals exhibit different affinity/attraction for sorption sites hence some of the ions will be adsorbed over others. The statement agrees with the results of the current study as Fe and Mn (except for ordinary biochars) were adsorbed onto biochar surfaces after 1 contact time while Al, Cu, Ni, and Mn (except for activated biochars) indicated the desorption of these heavy metal ions. Available ions in AMD solution at varying concentrations will result in competition for attachment onto biochar surface matrix adsorption sites which affect the adsorption efficiencies of these heavy metal ions (Zhang, *et al.*, 2016). In a nutshell, it can be concluded that biochar from phytoremediation biomasses did not prove to be a good adsorbent for the efficient removal of heavy metals from acid mine drainage solution.

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Table 4.13a. Effect of contact time on Al, Cu, Fe, Ni, and Mn adsorption in acid mine drainage by ordinary biochars from phytoremediation and non-phytoremediation biomasses.

Al							Cu					
Ordinary biochar			Activated biochar				Ordinary biochar			Activated biochar		
Sample code	Qeh (mg/g)	Contact time at Qeh (hr)	R (%)	Qeh (mg/g)	Contact time at Qeh (hr)	R (%)	Qeh (mg/g)	Contact time at Qeh (hr)	R (%)	Qeh (mg/g)	Contact time at Qe h(hr)	R (%)
BCV1	0.13	0.5	2.7	0.35	0.5	7.38	-0.01	0.30	-4.60	0.00	0.50	0.00
BCV2	-0.18	0.5	-3.79	0.3	0.5	6.27	-0.12	0.30	-51.72	-0.02	0.50	-6.90
BCC1	0.16	2	3.29	0.07	2	1.45	0.00	0.30	0.00	-0.01	0.50	-6.32
BCC2	-0.23	2	-4.87	0.15	0.5	3.15	-0.05	0.50	-22.99	-0.10	2.00	-44.83
BCL1	-0.25	2	-5.29	0.3	2	6.27	-0.01	2.00	-5.17	0.00	2.00	0.00
BCL2	0.3	0.5	6.29	0.17	2	3.62	0.00	0.50	0.00	-0.01	1.00	-3.45

Fe							Ni					
Ordinary biochar			Activated biochar				Ordinary biochar			Activated biochar		
Sample code	Qeh (mg/g)	Contact time at Qeh (hr)	R (%)	Qeh (mg/g)	Contact time at Qeh (hr)	R (%)	Qeh (mg/g)	Contact time at Qeh (hr)	R (%)	Qeh (mg/g)	Contact time at Qeh (hr)	R (%)
BCV1	4.95	0.30	13.97	4.86	4.00	13.71	-0.19	0.30	-6.63	-0.27	4.00	-9.52
BCV2	3.68	8.00	10.38	5.16	4.00	14.56	-0.33	8.00	-11.48	-0.25	4.00	-8.59
BCC1	4.59	4.00	12.94	3.63	8.00	10.22	-0.33	4.00	-11.48	-0.26	8.00	-12.65
BCC2	4.54	4.00	12.79	4.01	8.00	11.32	-0.30	4.00	-10.41	-0.32	8.00	-11.16
BCL1	4.16	4.00	11.72	3.98	8.00	11.21	-0.38	4.00	-13.35	-0.35	8.00	-12.00
BCL2	3.83	8.00	10.83	4.12	8.00	11.63	-0.34	8.00	-12.04	-0.31	8.00	-10.88

Qe : maximum equilibrium adsorption capacity and R (%): percentage removal efficiency, BCV1= *Chrysopogon zizanioides* non-phytoremediation biochar, BCV2:*Chrysopogon zizanioides* phytoremediation biochar, BCC1: *Cymbopogon nardus* non-phytoremediation biochar, BCC2: *Cymbopogon nardus* phytoremediation biochar, BCL1: *Cymbopogon citratus* non-phytoremediation biochar, BCL2: *Cymbopogon citratus* phytoremediation biochar. ACBCV1: activated *Chrysopogon zizanioides* non-phytoremediation biochar, ACBCV2: activated *Chrysopogon zizanioides* phytoremediation biochar, ACBCC1: activated *Cymbopogon nardus* non-phytoremediation biochar, ACBCC2: activated *Cymbopogon nardus* phytoremediation biochar, ACBCL1:activated *Cymbopogon citratus* non-phytoremediation biochar, ACBCL2: activated *Cymbopogon citratus* phytoremediation biochar.

Table 4.13b. Effect of contact time on Al, Cu, Fe, Ni, and Mn adsorption in acid mine drainage by ordinary biochars from phytoremediation and non-phytoremediation biomasses (continuation)

Sample code	Mn					
	Ordinary biochar			Activated biochar		
	Q _{eh} (mg/g)	Contact time at Q _{eh} (hr)	R (%)	Q _{eh} (mg/g)	Contact time at Q _{eh} (hr)	R (%)
BCV1	0.19	0.30	2.26	0.04	4.00	4.33
BCV2	0.37	2.00	4.30	0.11	0.5	1.32
BCC1	-0.09	2.00	-1.11	-0.08	0.5	-0.93
BCC2	-0.03	2.00	-0.40	0.14	0.5	1.63
BCL1	-0.16	2.00	-1.88	-0.11	8.00	-1.33
BCL2	0.15	2.00	1.77	-0.24	4.00	-1.11

Q_e :maximum equilibrium adsorption capacity and R (%) : percentage removal efficiency, BCV1: *Chrysopogon zizanioides* non-phytoremediation biochar, BCV2: *Chrysopogon zizanioides* phytoremediation biochar, BCC1: *Cymbopogon nardus* non-phytoremediation biochar, BCC2: *Cymbopogon nardus* phytoremediation biochar, BCL1: *Cymbopogon citratus* non-phytoremediation biochar, BCL2: *Cymbopogon citratus* phytoremediation biochar. Q_{e,max} :maximum equilibrium adsorption capacity and R(%): percentage removal efficiency.

4.5.3 Effect of biochar dosage on nitrate and phosphate adsorption by ordinary biochars and activated biochars from non-phytoremediation and phytoremediation biomasses

Generally, the adsorption performance for PO₄³⁻ and NO₃⁻ ions by ordinary and activated biochars increased with an increase in biochar dosage until most of the graphs were constant at 0.04g dosage as depicted in Figure 4.13. Biochars from phytoremediation biomasses displayed higher adsorption capacities for PO₄³⁻ and NO₃⁻ ions as a function of biochar dosage compared to the counterparts, this could be attributed to the strong attraction of PO₄³⁻ and NO₃⁻ ions into biochar's matrix by biochar's impregnated heavy metals. The report by Wang *et al.* (2021), elucidates that increasing biochar dosage increases reactive functional groups and contact area for adsorbate hence enhancing its removal rate. In comparison, ordinary biochars indicated a low PO₄³⁻ adsorption capacity range between 6.74 and 14.13 mg g⁻¹ as compared to activated biochars which ranged between 16.72 and 19 mg g⁻¹. Activated biochars also had a higher NO₃⁻ equilibrium adsorption capacity range between 16.44 and 25.39 mg g⁻¹ compared to ordinary

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biochars which ranged from 9.75 and 20.72 mg g⁻¹. The differences in adsorption performance between ordinary and activated biochars could be accounted to the difference in their porosity. SEM analysis data indicated that activated biochars appeared to have more porous structures as opposed to ordinary biochars.

Table 4.14 indicates that percentage removal efficiencies for PO₄³⁻ ion descended as follows; 59.06> 56.54> 55.75>54.50> 27.20> 26.97 % as function of biochar dosage corresponding to BCC2, BCV2, BCC1, BCV1, BCL2 and BCL1, respectively. Removal percentage efficiencies of PO₄³⁻ ion by activated biochars decreased in the following order: 76.05>75.07>73.32>72.95>66.92>28.96 corresponding to BCC2, BCV1, BCC1, BCV2, BCL1, and BCL2, respectively. Percentage removal efficiencies of NO₃⁻ ion by ordinary biochars indicated the following descending order; BCC2 (64.65%)>BCV2 (58.32%)>BCC1 (57.63%)>BCV1 (56.00%)>BCL2 (45.0%)>BCL1 (27.94%), respectively. Activated biochars showed a decrease of NO₃⁻ ion percentage removal efficiencies as follows; BCC2 (72.56%)>BCC1 (60.13%)>BCV2 (59.41%)>BCV1 (57.03%)>BCL2 (50.14%)>BCL1 (46.99%), respectively.

Activated biochars had higher PO₄³⁻ and NO₃⁻ adsorption compared to ordinary biochars, activated *Cymbopogon nardus* phytoremediation biochar displayed the highest adsorption capacities for both PO₄³⁻ and NO₃⁻ ions. This could be attributed to the high surface porosity of the biochar due to ZnCl₂ activation as depicted in Figure 4.10 which enables the physical deposition of phosphate and nitrate ions onto the biochar matrix. It should be noted that ion adsorption is not only influenced by net surface charges and porosity but also is affected by other factors such as specific surface area, the variation in adsorption capacities of

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PO_4^{3-} and NO_3^- ions between biochar samples could be attributed to the difference in their surface chemistry and morphology. According to Jing *et al.* (2014), an increase in adsorption capacities after activation could be partly attributed to the increase in the specific surface area of the adsorbent.

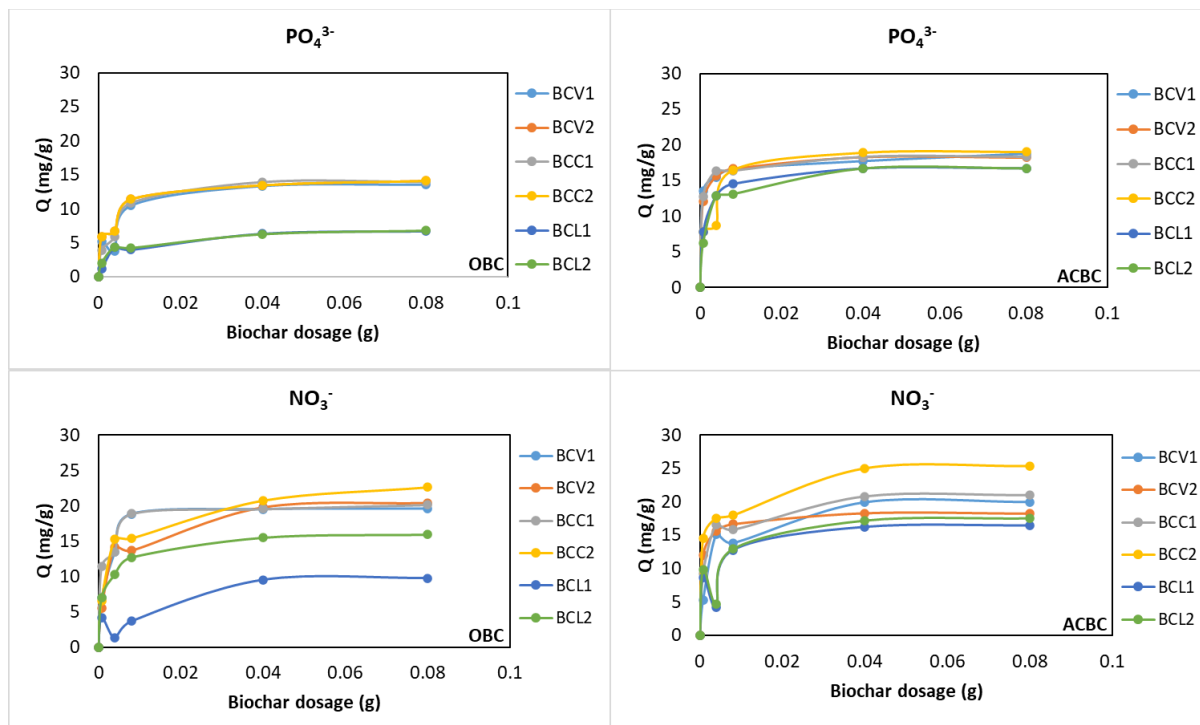


Figure 4.13 Effect of biochar dosage on PO_4^{3-} and NO_3^- adsorption in artificial co-existence of PO_4^{3-} and NO_3^- wastewater by ordinary and activated biochars from non-phytoremediation and phytoremediation biomasses. BCV1: *Chrysopogon zizanioides* non-phytoremediation biochar, BCV2: *Chrysopogon zizanioides* phytoremediation biochar, BCC1: *Cymbopogon nardus* non-phytoremediation biochar, BCC2: *Cymbopogon nardus* phytoremediation biochar, BCL1: *Cymbopogon citratus* non-phytoremediation biochar, BCL2: *Cymbopogon citratus* phytoremediation biochar.

Table 4.14. Effect of biochar dosage on the adsorption of PO_4^{3-} and NO_3^- in artificial co-existence of PO_4^{3-} and NO_3^- wastewater by ordinary and activated biochars from non-phytoremediation and phytoremediation biomasses.

PO_4^{3-}						
Ordinary biochar				Activated biochar		
Sample code	Qeh (mg/g)	Dosage at Qeh (g)	R (%)	Qeh (mg/g)	Dosage at Qeh (g)	R (%)
BCV1	13.57	0.08	54.50	18.76	0.008	75.07
BCV2	14.12	0.08	56.54	18.28	0.04	72.95
BCC1	13.92	0.08	55.75	18.31	0.08	73.32
BCC2	14.13	0.08	59.06	19	0.08	76.05
BCL1	6.74	0.08	26.97	16.78	0.04	66.92
BCL2	6.79	0.08	27.20	7.24	0.08	28.96

NO_3^-						
Ordinary biochar				Activated biochar		
Sample code	Qeh (mg/g)	Dosage at Qeh (g)	R (%)	Qeh(mg/g)	Dosage at Qeh (g)	R (%)
BCV1	19.58	0.08	56.00	19.9	0.08	57.03
BCV2	20.39	0.08	58.32	20.79	0.08	59.41
BCC1	20.15	0.08	57.63	21.04	0.08	60.13
BCC2	20.72	0.04	64.65	25.39	0.08	72.56
BCL1	9.75	0.08	27.94	16.44	0.08	46.99
BCL2	15.9	0.08	45.0	17.54	0.08	50.14

Qeh :highest equilibrium adsorption capacity and R (%) : percentage removal efficiency, BCV1: *Chrysopogon zizanioides* non-phytoremediation biochar, BCV2: *Chrysopogon zizanioides* phytoremediation biochar, BCC1: *Cymbopogon nardus* non-phytoremediation biochar, BCC2: *Cymbopogon nardus* phytoremediation biochar, BCL1: *Cymbopogon citratus* non-phytoremediation biochar, BCL2: *Cymbopogon citratus* phytoremediation biochar. $Q_{\text{e max}}$: maximum equilibrium adsorption capacity and R(%):percentage removal efficiency.

4.5.4 Effect of solution pH on PO_4^{3-} and NO_3^- adsorption by ordinary biochars and activated biochars from non-phytoremediation and phytoremediation biomasses

The solution pH is a vital factor regarding the adsorption experiments since it affects the protonation and deprotonation of functional groups, surface charges density, diffusion rate, and chemical speciation forms of adsorbate (Hafshejani *et al.*, 2016). Most of the biochar samples showed an increase of PO_4^{3-} and NO_3^- ions adsorptions with an increasing solution pH until pH 8 where the graphs decreased up to solution pH 12 as shown in Figure 4.14. This

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observation coincides with the study by (Yin *et al.*, 2018) on NO_3^- adsorption, as they found that nitrate adsorption by Al-activated biochar increased as pH was increased from pH 2 to 6 where optimum adsorption (saturation) was reached and the graph gradually decreased with further increase of solution pH. A decrease in adsorption with a further increase in pH could be attributed to the competition between hydroxide (OH^-) ions with PO_4^{3-} and NO_3^- ions for adsorption sites on biochar surfaces under alkaline conditions which decrease the adsorption capacities of PO_4^{3-} and NO_3^- ions (Yin *et al.*, 2018). PO_4^{3-} adsorption of ordinary *C. zizanioides* phytoremediation biochar decreased gradually from pH 2 to 4 and increased gradually until solution pH 12.

Biochars from non-phytoremediation biomasses indicated higher phosphate and nitrate adsorption capacities because of solution pH compared to biochars from non-phytoremediation biomasses. Activated *Cymbopogon nardus* non-phytoremediation biochar displayed the highest phosphate and nitrate adsorptions as compared to other samples. The pzc data in Table 4.15 indicate that non-phytoremediation biochars showed a higher deviation of ambient solution pH values from pH_{pzc} as compared to phytoremediation biochars. This suggests that based on the electrostatic attraction of ions mechanism, biochars from non-phytoremediation biomasses will have a higher potential to adsorb phosphate and nitrate ions as compared to phytoremediation biochars due to their highly protonated surfaces. Generally activated biochar samples showed lower phosphate and nitrate adsorption capacities as a function of solution pH compared to ordinary biochar samples. This observation is supported by pzc data reported in table 4.8 which indicates that ZnCl_2 activation reduced the magnitude of positive charges available to adsorb nitrate and phosphate ions.

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Ordinary *C. zizanioides* non-phytoremediation biochar indicated a gradual increase of PO_4^{3-} adsorption from solution pH 2 to 4 and the adsorption decreased until pH 8 and increased again up to solution pH 12. PO_4^{3-} adsorption by ordinary *C. nardus* non-phytoremediation biochar showed a slowly decreasing rate from pH 2 to 4 and increased gradually until pH 6 where the graph decreased constantly until solution pH 12. Activated *C. nardus* and *C. citratus* showed an increase in adsorption of PO_4^{3-} adsorption with an increase of solution pH until 6 and a decrease around pH 7 until pH 12 for *C. citratus* and pH 10 for *C. nardus* where an increase was again observed from pH 10 to 12. The activated *C. citratus* and *C. zizanioides* showed a fluctuating trend of PO_4^{3-} adsorption between solution pH 2 and 12. PO_4^{3-} adsorption by activated *C. zizanioides* was constant from solution pH 2 to 4 and decreased at a slow rate until pH 6 where the graph gradually increased up to pH 10 and decreased again until solution pH 12.

Ordinary *C. zizanioides* non-phytoremediation biochar had an increasing NO_3^- adsorption from solution pH 2 to 6 and decreased until pH 10 and finally increased again until pH 12. Activated *C. zizanioides* indicated a gradual decrease of NO_3^- from solution pH 2 to 4 and slightly increased from pH 4 to 6. The graph slightly decreased again up to pH 8 and finally increased up to pH 12. Table 4.15 shows that PO_4^{3-} adsorption ranged between 20.97 and 36.12 mg g^{-1} for biochar samples while activated biochars indicated a range between 24.31 and 38.93 mg g^{-1} . On the other side, ordinary biochars had a range between 21.19 and 36.12 mg g^{-1} of NO_3^- equilibrium adsorption while activated biochars indicated NO_3^- equilibrium adsorption range between 22.69 and 37.47 mg g^{-1} . At a low pH range, protonation reactions induce positive charges on the biochar surface, increasing the electrostatic attraction between negatively charged adsorbates and positively charged biochar surfaces (Chintala *et al.*, 2013).

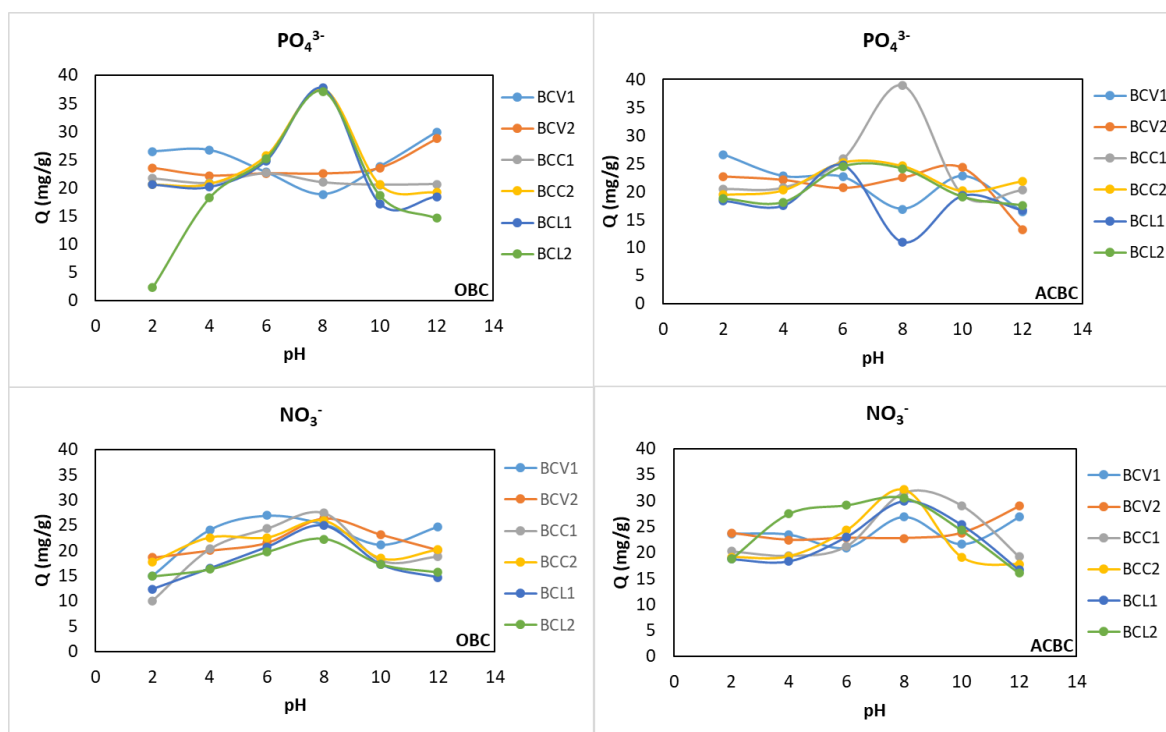


Figure 4.14. Effect of solution pH on PO_4^{3-} and NO_3^- adsorption in artificial co-existence of PO_4^{3-} and NO_3^- wastewater by ordinary and activated biochars from non-phytoremediation and phytoremediation biomasses. BCV1: *Chrysopogon zizanioides* non-phytoremediation biochar, BCV2: *Chrysopogon zizanioides* phytoremediation biochar, BCC1: *Cymbopogon nardus* non-phytoremediation biochar, BCC2: *Cymbopogon nardus* phytoremediation biochar, BCL1: *Cymbopogon citratus* non-phytoremediation biochar, BCL2: *Cymbopogon citratus* phytoremediation biochar. Q_{max} : maximum equilibrium adsorption capacity and R(%): percentage removal efficiency.

Among ordinary biochars, PO_4^{3-} percentage removal indicated a decreasing order as follows; BCC1 (46.23%) > BCV2 (58.69%) > BCV1 (61.66%) > BCL2 (75.86%) > BCC2 (76.71%) > BCL1 (77.06%), respectively as a function of solution pH. Activated biochars indicated an increasing order of PO_4^{3-} percentage removal as follows; BCV2 (49.66%) < BCL2 (50.00%) < BCL1 (50.50%) < BCC2 (51.48%) < BCV1 (54.34%) < BCC1 (79.48%), respectively. The NO_3^- percentage removal amongst ordinary biochars decreased as follows; 73.61 > 73.41 > 59.14 > 58.87 > 54.55 > 43.06 % corresponding to BCC2, BCL1, BCL2, BCV2, BCV1 and BCC1, respectively. On the other side, it was observed that activated biochars NO_3^- percentage removal amongst activated biochars ascended as follows; BCL2 (46.11%)

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<BCL1(46.24%) <BCV2 (47.10%) <BCC2(48.09%) <BCV1 (50.75%) <BCC1 (76.16%), respectively. It should be noted that at solution pH above the point of zero charges of the adsorbent, it is expected that there would be no adsorption of anions onto biochar surfaces since the adsorbent would have developed negative charges resulting in electrostatic repulsion between anions and biochars Van der Waals interaction correlating to the higher surface area of the adsorbent. Nevertheless, it was observed that PO_4^{3-} and NO_3^- ions were adsorbed on the surfaces of some biochars at solution pH above their pzc values. A similar observation was

Table 4.15. Effect of solution pH on the adsorption of PO_4^{3-} and NO_3^- in artificial co-existence of PO_4^{3-} and NO_3^- wastewater by ordinary and activated biochars from non-phytoremediation and phytoremediation biomasses.

PO_4^{3-}						
Ordinary biochar				Activated biochar		
Sample code	Qeh (mg/g)	pH at Qeh	R (%)	Qeh (mg/g)	pH at Qeh	R (%)
BCV1	29.91	12	61.06	26.62	2	54.34
BCV2	28.75	12	58.69	24.31	10	49.66
BCC1	20.97	8	46.23	38.93	8	79.48
BCC2	37.58	8	76.71	25.21	6	51.48
BCL1	37.75	8	77.06	24.77	6	50.50
BCL2	37.16	8	75.86	24.49	6	50.00
NO_3^-						
Ordinary biochar				Activated biochar		
Sample code	Qeh (mg/g)	pH at Qeh	R (%)	Qeh (mg/g)	pH at Qeh	R (%)
BCV1	26.40	12	54.55	26.90	8	50.75
BCV2	26.96	12	58.87	23.18	10	47.10
BCC1	21.19	6	43.06	37.47	8	76.16
BCC2	36.12	8	73.41	23.58	6	48.09
BCL1	35.94	8	73.05	22.75	6	46.24
BCL2	29.1	8	59.14	22.69	6	46.11

Qeh : highest equilibrium adsorption capacity and R (%) : percentage removal efficiency, BCV1: *Chrysopogon zizanioides* non-phytoremediation biochar, BCV2: *Chrysopogon zizanioides* phytoremediation biochar, BCC1: *Cymbopogon nardus* non-phytoremediation biochar, BCC2= *Cymbopogon nardus* phytoremediation biochar, BCL1: *Cymbopogon citratus* non-phytoremediation biochar, BCL2: *Cymbopogon citratus* phytoremediation biochar. $Q_{e_{\max}}$:maximum equilibrium adsorption capacity and R(%):percentage removal efficiency.

reported in the study carried out by (Ip *et al.*, 2009) as they observed that negatively charged bamboo adsorbed negatively charged reactive dye and the study suggested that the adsorption

could be attributed to π - π interaction and Van der Waals interaction correlating to the higher surface area of the adsorbent.

4.5.5 Effect of contact time on PO_4^{3-} and NO_3^- adsorption by ordinary biochars and activated biochars from non-phytoremediation and phytoremediation biomasses

To estimate the feasibility and efficacy of an adsorbent for its utilization in pollution remediation, the time required to reach equilibrium adsorption capacity is a crucial factor to consider (Mishra *et al.*, 2014). Figure 4.15 indicates that the graphs of PO_4^{3-} and NO_3^- ions adsorption became constant after 1hr contact time for most of the biochar samples. Ordinary *C. zizanioides* and *C. citratus* non-phytoremediation biochars showed increased adsorption of PO_4^{3-} from 0.3hr and 0.5hr contact times the graphs decreased until graphs were constant at 1hr and 2hr, respectively. Activated *C. zizanioides* indicated a rapid PO_4^{3-} adsorption from 0.5hr to 1hr contact times and decreased until the graph leveled off at 2hr contact time. Activated *C. zizanioides* non-phytoremediation biochar showed an increase of NO_3^- adsorption from 0.5hr to 1hr, the graph slightly decreased and increased until 4hr contact and decreased. No significant changes in equilibrium concentrations with further increase of contact time imply that the adsorbates have occupied all adsorption sites.

Table 4.16 indicates the equilibrium adsorption capacities due to the contact time effect, PO_4^{3-} adsorption capacities of ordinary biochars ranged from 18.27 mg g^{-1} to 36.58 mg g^{-1} while activated biochars range between 17.05 and 27.66 mg g^{-1} . Ordinary *C. zizanioides* non-phytoremediation biochar had the highest PO_4^{3-} percentage removal (74.52%) as compared to other biochars. Ordinary biochar samples displayed a NO_3^- adsorption capacity range of 16.50-21.68 mg g^{-1} while activated biochar samples displayed a range between 15.48 and 28.64 mg g^{-1} .

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¹. Activated *C. zizanioides* had the highest NO_3^- percentage removal (58.28%) as compared to other biochar samples.

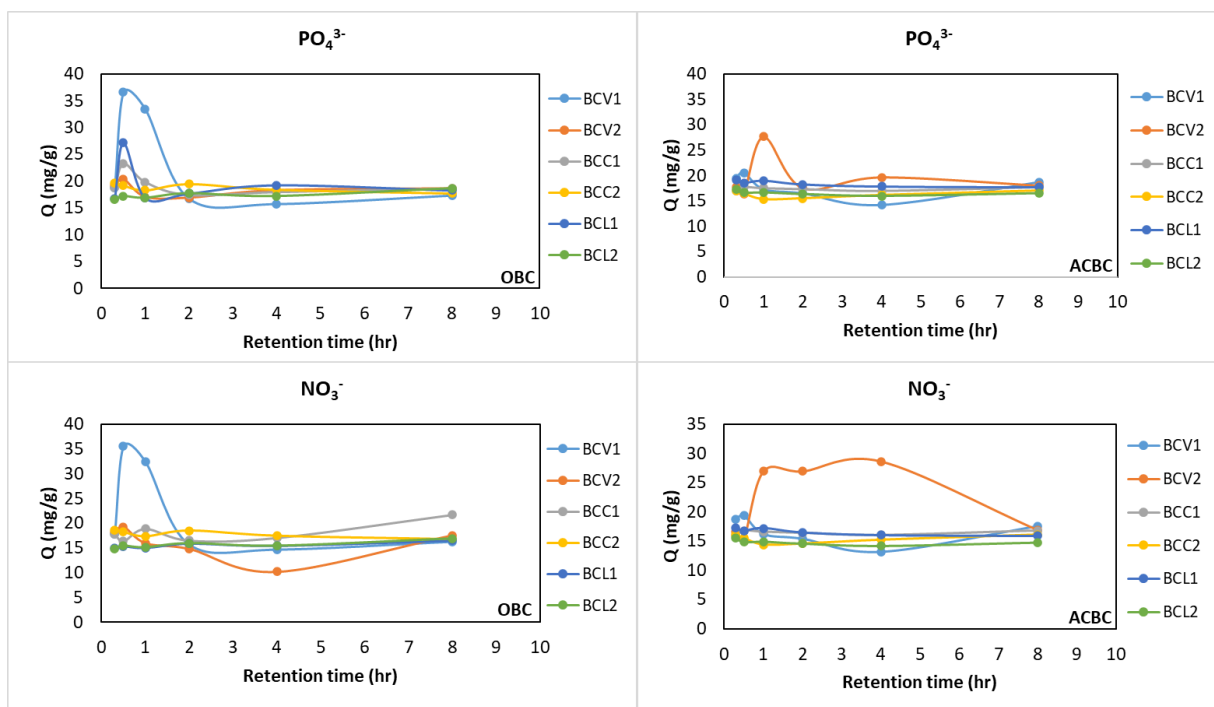


Figure 4.15. Effect of contact time on PO_4^{3-} and NO_3^- adsorption in artificial co-existence of PO_4^{3-} and NO_3^- wastewater by ordinary and activated biochars from non-phytoremediation and phytoremediation biomasses. BCV1: *Chrysopogon zizanioides* non-phytoremediation biochar, BCV2: *Chrysopogon zizanioides* phytoremediation biochar, BCC1: *Cymbopogon nardus* non-phytoremediation biochar, BCC2: *Cymbopogon nardus* phytoremediation biochar, BCL1: *Cymbopogon citratus* non-phytoremediation biochar, BCL2: *Cymbopogon citratus* phytoremediation biochar. OBC: ordinary biochar, ACBC: activated biochar.

Table 4.16. Effect of contact time on the adsorption of PO_4^{3-} and NO_3^- in artificial co-existence of PO_4^{3-} and NO_3^- wastewater by ordinary and activated biochars from non-phytoremediation and phytoremediation biomasses.

PO_4^{3-}						
Sample code	Ordinary biochar			Activated biochar		
	Qeh (mg/g)	Contact time at Qeh (hr)	R (%)	Qeh (mg/g)	Contact time at Qeh (hr)	R (%)
BCV1	36.58	0.50	74.52	20.46	0.50	41.68
BCV2	20.36	0.50	41.47	27.66	1.00	56.33
BCC1	23.32	0.50	46.08	17.74	8.00	36.13
BCC2	19.57	0.30	39.87	17.05	8.00	34.73
BCL1	18.27	8.00	37.22	19.04	8.00	38.78
BCL2	18.65	8.00	37.99	17.25	0.50	35.14
NO_3^-						
Sample code	Ordinary biochar			Activated biochar		
	Qeh (mg/g)	Contact time at Qeh (hr)	R (%)	Qeh (mg/g)	Contact time at Qeh	R (%)
BCV1	18.62	0.3	38.02	19.39	0.50	39.45
BCV2	19.23	0.50	39.23	28.64	4.00	58.28
BCC1	21.68	8.00	44.11	16.79	8.00	34.17
BCC2	18.63	0.30	38.02	16.11	8.00	32.77
BCL1	16.50	8.00	33.58	17.26	0.30	35.12
BCL2	16.88	8.00	34.34	15.48	0.30	31.49

Qeh : highest equilibrium adsorption capacity and R (%): percentage removal efficiency. BCV1: *Chrysopogon zizanioides* non-phytoremediation biochar, BCV2: *Chrysopogon zizanioides* phytoremediation biochar, BCC1: *Cymbopogon nardus* non-phytoremediation biochar, BCC2: *Cymbopogon nardus* phytoremediation biochar, BCL1: *Cymbopogon citratus* non-phytoremediation biochar, BCL2: *Cymbopogon citratus* phytoremediation biochar.

4.5.6 Effect of initial concentration of PO_4^{3-} and NO_3^- in artificial wastewater on their adsorption by ordinary biochars and activated biochars from non-phytoremediation and phytoremediation biomasses

Figure 4.16 indicate that PO_4^{3-} and NO_3^- adsorption increased with increasing initial concentrations until the graphs leveled off at 300 mg l^{-1} . Ordinary *C. citratus* non-phytoremediation biochar showed an increase of PO_4^{3-} adsorption from 20 mg l^{-1} to 50 mg l^{-1} and slightly decreased until 100 mg l^{-1} initial concentration and increased up to 200 mg l^{-1} and decreased slightly until 300 mg l^{-1} and finally increased rapidly.

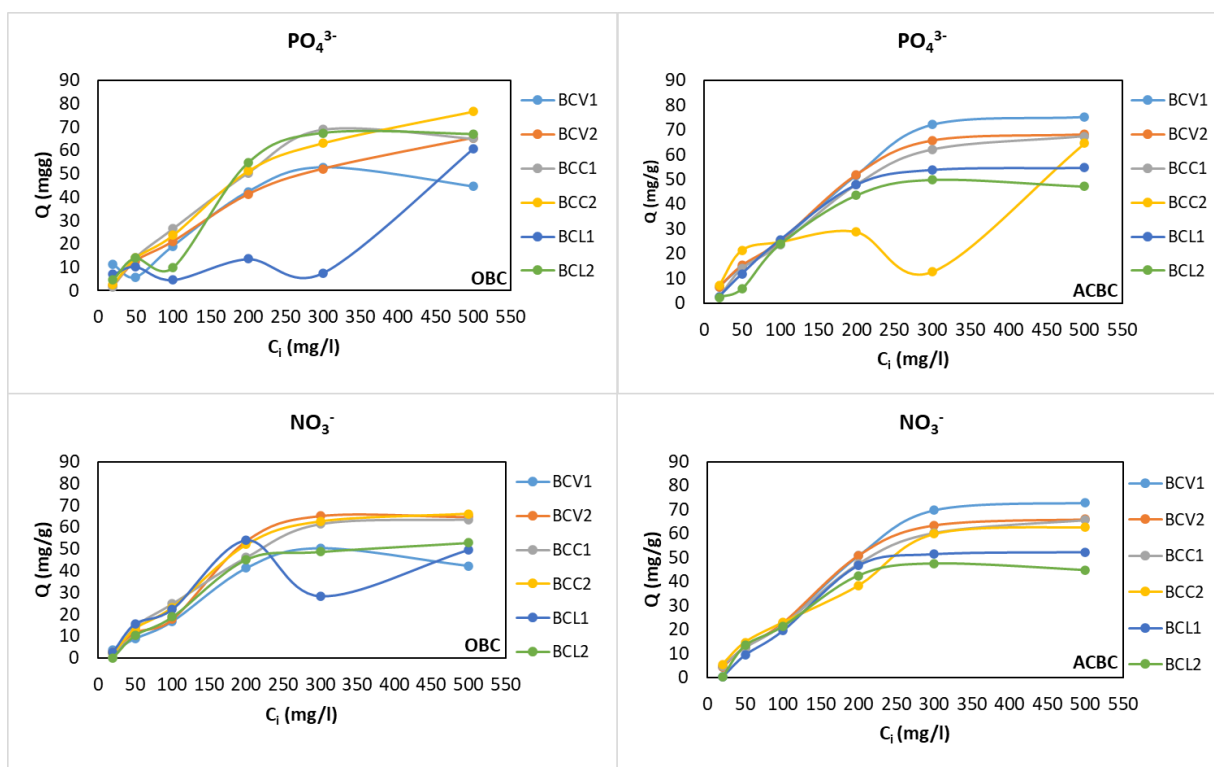


Figure 1.16. Effect of initial concentration of PO_4^{3-} and NO_3^- in artificial co-existence of PO_4^{3-} and NO_3^- wastewater on the adsorption of PO_4^{3-} and NO_3^- by ordinary and activated biochars from non-phytoremediation and phytoremediation biomasses. BCV1: *Chrysopogon zizanioides* non-phytoremediation biochar, BCV2: *Chrysopogon zizanioides* phytoremediation biochar, BCC1: *Cymbopogon nardus* non-phytoremediation biochar, BCC2: *Cymbopogon nardus* phytoremediation biochar, BCL1: *Cymbopogon citratus* non-phytoremediation biochar, BCL2: *Cymbopogon citratus* phytoremediation biochar. OBC: ordinary biochar, ACBC: activated biochar.

Activated *C. nardus* phytoremediation biochar showed an increasing trend of PO_4^{3-} adsorption from 20 mg l^{-1} up to 200 mg l^{-1} where the graph dropped until 300 mg l^{-1} and the adsorption increased. Ordinary *C. citratus* non-phytoremediation biochar showed an increasing trend of NO_3^- adsorption from 20 mg l^{-1} to 200 mg l^{-1} where the adsorption decreased until 300 mg l^{-1} and finally increased again. Table 4.17 shows that PO_4^{3-} adsorption capacities of ordinary biochar samples ranged between 52.73 and 76.65 mg l^{-1} while activated biochar samples ranged from 42.29 to 75.19 mg l^{-1} . The expectation is that ion adsorption will increase with an increasing initial concentration of the adsorbate (Elaigwu *et al.*, 2010), the current results agree with the

phenomenon. Increasing concentration entails more availability of molecules to compete for adsorption sites on the surface of the adsorbent hence enhancing the adsorption capacity of the adsorbate until the stationary adsorption phase is reached.

Table 1.17 Effect of initial concentration of PO_4^{3-} and NO_3^- in artificial co-existence of PO_4^{3-} and NO_3^- wastewater on the adsorption of PO_4^{3-} and NO_3^- by ordinary and activated biochars from non-phytoremediation and phytoremediation biomasses.

PO_4^{3-}						
Ordinary biochar				Activated biochar		
Sample code	Qeh (mg/g)	Initial conc. at Qeh (mg/l)	R (%)	Qeh (mg/g)	Initial conc. at Qeh (mg/l)	R (%)
BCV1	52.73	300.00	17.58	75.19	500.00	15.08
BCV2	65.28	300.00	21.76	49.86	300.00	13.69
BCC1	69.06	300.00	23.02	67.38	500.00	13.51
BCC2	76.65	500.00	13.07	64.50	500.00	12.93
BCL1	60.56	500.00	15.37	54.70	500.00	10.97
BCL2	67.47	300.00	17.46	68.26	500.00	9.45
NO_3^-						
Ordinary biochar				Activated biochar		
Sample code	Qeh (mg/g)	Initial conc. at Qeh (mg/l)	R (%)	Qeh (mg/g)	Initial conc. at Qeh (mg/l)	R (%)
BCV1	42.29	300.00	14.10	72.91	300.00	23.41
BCV2	65.19	300.00	21.87	65.97	500.00	13.24
BCC1	63.43	500.00	12.73	65.65	500.00	13.18
BCC2	66.15	500.00	15.29	62.76	500.00	12.60
BCL1	49.58	20.00	24.79	52.32	500.00	10.50
BCL2	52.90	500.00	12.63	44.75	500.00	8.98

Qeh :highest equilibrium adsorption capacity, conc:initial concentration, and R (%) : percentage removal efficiency. BCV1: *Chrysopogon zizanioides* non-phytoremediation biochar, BCV2: *Chrysopogon zizanioides* phytoremediation biochar, BCC1: *Cymbopogon nardus* non-phytoremediation biochar, BCC2:*Cymbopogon nardus* phytoremediation biochar, BCL1: *Cymbopogon citratus* non-phytoremediation biochar, BCL2: *Cymbopogon citratus* phytoremediation biochar.

4.6 Adsorption isotherms of PO_4^{3-} and NO_3^- in a binary system

Adsorption capacities of PO_4^{3-} by ordinary biochar samples showed a decreasing order as follows; BCC2 (76.65 mg g⁻¹)>BCC1 (69.06 mg g⁻¹)>BCL2 (67.47 mg g⁻¹)>BCV2 (65.28 mg g⁻¹)>BCL1(60.56 mg g⁻¹)>BCV1 (52.73 mg g⁻¹), respectively as indicated in Table 4.18a.

Activated biochar samples indicated a descending order of PO_4^{3-} adsorption as follows; BCV1

Results and Discussion

(76.19 mg g⁻¹)>BCL2 (68.26 mg g⁻¹)>BCC1 (67.38 mg g⁻¹)>BCL1 (54.50 mg g⁻¹)>BCV2 (49.86 mg g⁻¹), respectively. NO₃⁻ adsorption capacities of ordinary biochars ascended in the following order: 42.29<49.58<52.90<63.43<65.19<66.15 mg g⁻¹ corresponding to BCV1, BCL1, BCL2, BCC1, BCV2, and BCC2, respectively.

Activated biochar samples indicated the following increasing order of NO₃⁻ adsorption capacities; 44.75<52.32<62.76<65.65<65.67<72.91 corresponding to BCL2, BCL1, BCC2, BCC1, BCV2 and BCV1, respectively. The correlation coefficients and constant values are listed in Table 4.18a & b. Eleven biochars (11) followed Temkin adsorption isotherm, initial concentrations of 5 biochars were best fitted in the Dubinin-Radushkevich isotherm. Three (3) biochars followed Langmuir 1 and the other 5 biochars were best fitted in Langmuir 2. Langmuir 2 showed a correlation coefficient of 0.67 for PO₄³⁻ adsorption. Dubinin-Radushkevich indicated higher correlations (PO₄³⁻: 0.92-0.96 and NO₃⁻:0.91-0.99) followed by Langmuir 1 (PO₄³⁻: 0.86-1 and NO₃⁻:0.67-1) and Temkin (PO₄³⁻:0.32-0.98 and NO₃⁻:0.33-0.97) for phosphate and nitrate adsorption. According to (Karthikeyan and Meenakshi, 2019), the superiority of fitness of the adsorption processes is indicated by a higher correlation coefficient value (R²).

Table 4.18a. Correlation factors (R^2) from adsorption isotherm plots generated in this study.
 PO_4^{3-} adsorption

	LG 1	LG 2	LG 3	LG 4	Freunlich	Temkin	Dubinin-Radushkevich
Sample code	R^2						
BCV1	0.98	0.98	0.52	0.52	0.93	0.94	0.67
BCV2	0.86	0.86	0.00	0.00	0.82	0.79	0.57
BCC1	0.82	0.08	0.00	0.00	0.83	0.95	0.96
BCC2	0.90	0.90	0.01	0.01	0.90	0.97	0.90
BCL1	0.07	0.07	0.01	0.01	0.31	0.32	0.08
BCL2	0.90	0.90	0.04	0.04	0.90	0.98	0.91
ACBCV1	1.00	1.00	0.72	0.72	0.97	0.92	0.70
ACBCV2	1.00	1.00	0.78	0.78	0.96	0.94	0.73
ACBCC1	0.89	0.89	0.02	0.02	0.89	0.84	0.92
ACBCC2	0.67	0.67	0.12	0.12	0.44	0.41	0.53
ACBCL1	0.00	0.00	0.13	0.13	0.37	0.70	0.18
ACBCL2	0.98	0.98	0.06	0.06	0.87	0.90	0.75

LG: Langmuir, AC:activated, BCV1: *Chrysopogon zizanioides* non-phytoremediation biochar, BCV2: *Chrysopogon zizanioides* phytoremediation biochar, BCC1:*Cymbopogon nardus* non-phytoremediation biochar, BCL1: *Cymbopogon citratus*, non-phytoremediation biochar, BCL2: *Cymbopogon citratus* phytoremediation biochar.

The biochars that best fitted the Langmuir 1 and 2 are: BCV1, BCV2, activated BCV1, activated BCV2, and activated BCC2 for PO_4^{3-} adsorption and BCV1, BCL2 and activated BCC2 for NO_3^- adsorption as shown in Table 4.18a. The maximum adsorption capacities for PO_4^{3-} that can be reached by BCV1, BCV2, activated BCV1, activated BCV2, and activated BCC2 are 62.99, 72.99, 113.64, 115.70, and 61.38 mg g^{-1} , respectively. BCV1, BCL2 and activated BCC2 can reach maximum adsorption of NO_3^- at 317.71, 294.7 and 99.42 mg g^{-1} , respectively (Table 4.18b). The Langmuir model explains the removal of adsorbate (s) by heterogeneous surfaces via chemical mechanisms (chemisorption) according to (Yin *et al.*,

2018).BCC2, BCL1, BCL2, activated BCL1 and BCL2 followed Temkin adsorption isotherm for PO_4^{3-} removal with possible maximum adsorptions at 101.74, 270.59, 123.07, 135.05, and 146.15 L g⁻¹, respectively. For NO_3^- adsorption, BCV2, BCC2, BCL1, activated BCV1, BCV2, and BCC1 also were best fitted in the Temkin adsorption equation with maximum possible adsorption capacities at 110.81, 101.39, 255.7, 106.00, 117.71 and 110.19 L g⁻¹, respectively. Temkin adsorption isotherm considers the indirect adsorbate interactions and states that there would be a linear decrease in the heat of adsorption of all molecules in the layer concerning coverage (Lalley *et al.*, 2016).

Table 4.18b. Correlation factors (R^2) from adsorption isotherm plots generated in this study.

Sample code	NO ₃ ⁻ adsorption						
	LG 1	LG 2	LG 3	LG 4	Freunlich	Temkin	Dubinin-Radushkevich
	R^2						
BCV1	1.00	1.00	0.07	0.07	0.92	0.85	0.74
BCV2	0.89	0.89	0.14	0.14	0.83	0.79	0.65
BCC1	0.78	0.78	0.08	0.08	0.71	0.94	0.99
BCC2	0.89	0.89	4E-05	4E-05	0.89	0.97	0.91
BCL1	0.03	0.03	0.00	0.00	0.30	0.33	0.08
BCL2	1.00	1.00	0.54	0.54	0.98	0.91	0.72
ACBCV1	0.99	0.99	0.19	0.19	0.96	0.93	0.76
ACBCV2	0.99	0.99	0.26	0.26	0.95	0.94	0.79
ACBCC1	0.82	0.82	0.03	0.03	0.80	0.97	0.97
ACBCC2	0.69	0.69	0.07	0.07	0.45	0.42	0.56
ACBCL1	0.82	0.82	0.15	0.15	0.76	0.92	0.98
ACBCL2	0.89	0.89	0.31	0.31	0.82	0.89	0.91

LG: Langmuir, AC:activated, BCV1: *Chrysopogon zizanioides* non-phytoremediation biochar, BCV2: *Chrysopogon zizanioides* phytoremediation biochar, BCC1:*Cymbopogon nardus* non-phytoremediation biochar, BCL1: *Cymbopogon citratus*, non-phytoremediation biochar, BCL2: *Cymbopogon citratus* phytoremediation biochar.

The Dubinin-Radushkevich adsorption isotherm was followed by BCC1 and activated BCC1 for PO_4^{3-} adsorption and BCC1, activated BCL2 for NO_3^- adsorption (Table 4.19). The maximum PO_4^{3-} adsorption capacity by BCC1 and activated BCC1 is 51.37 and 46.31 mg g^{-1} , respectively. The maximum NO_3^- adsorption capacities of BCC1, activated BCL1 and BCL2 correspond to 57.41, 42.42, and 32.26 mg g^{-1} , respectively. The Dubinin-Radushkevich adsorption isotherm confirms the physical attachment of adsorbate on the adsorbent structure (Banu *et al.*, 2020).

The K_L (Langmuir adsorption constant) represents the strength of adsorption, the data in Table 4.19 indicate a weak strength of adsorption values ranging from 0.007 to 0.046 L mg^{-1} . The heat of adsorption (K_T) constant from the Temkin adsorption model indicated a range between 0.006 and 0.024. Nandiyanto *et al.* (2020) associated low K_T values with minimal binding energy between the adsorbate and adsorbent. K_{ad} (free energy of adsorption) values from the Dubinin-Radushkevich adsorption model ranged between 0.001 and 0.004 mol^2/kJ^2 , the K_{ad} relates to the free energy of adsorption as the adsorbate diffuses from the ambient solution onto the adsorbent's surface (Olalekan *et al.*, 2013)

Table 4.19. Adsorption isotherm constants of PO_4^{3-} and NO_3^- removal by ordinary and activated biochars from non-phytoremediation and phytoremediation biomasses.

PO ₄ ³⁻ adsorption												
Isotherm model	Ordinary biochar						Activated biochar					
	BCV1	BCV2	BCC1	BCC2	BCL1	BCL2	BCV1	BCV2	BCC1	BCC2	BCL1	BCL2
Langmuir: linear eqn 1												
q _m (mg/g)	62.99	72.99					113.64					
K _L (L/mg)	0.01	0.00					0.00					
R ²	0.98	0.86					1.00					
Langmuir: linear eqn 2												
q _m (mg/g)								115.70		61.38		
K _L (L/mg)								0.00		0.01		
R ²								1.00		0.67		
Temkin												
b _T (L/mg)				101.74	270.59	123.07					135.05	146.18
K _T (J/mol)				0.00	0.00	0.00					0.00	0.00
R ²				0.97	0.32	0.98					0.70	0.90
Dubinin-Radushkevich												
q _m (mg/g)			51.37						46.31			
B (mol ² /kJ ²)			0.00						0.00			
R ²			0.96						0.92			
NO ₃ ⁻ adsorption												
Langmuir: linear eqn 2												
q _m (mg/g)	317.71					294.7				99.42		
K _L (L/mg)	0.00					0.00				0.01		
R ²	1					1.0				0.67		
Temkin												
b _T (L/mg)		110.81		101.39	255.78		106.00	117.71	110.19			
K _T (J/mol)		0		0	0		0	0	0			
R ²		0.79		0.97	0.33		0.93	0.94	0.97			
Dubinin-Radushkevich												
q _m (mg/g)			57.41								42.42	32.26
B (mol ² /kJ ²)			0.00								0.00	0.00
R ²			0.99								0.98	0.91

R²: correlation coefficient, eqn: equation, q_m: maximum adsorption capacity, b_T: Temkin isotherm equilibrium binding energy, K_L, K_T and K_{ad} are the Langmuir, Temkin and Dubinin-Radushkevich adsorption isotherm constants.

The highest correlation coefficients (R^2) in Table 4.18 and Table 4.19 indicate that sample best fit a particular adsorption model. The R^2 of samples that best fitted Langmuir models 1 and 2 discussed earlier in the report ranged between 0.67 and 1, while for the Temkin adsorption model, the R^2 values ranged from 0.32 to 0.98 and for Dubinin-Radushkevich adsorption the R^2 values ranged between 0.91 and 0.99. It can be concluded that the Dubinin-Radushkevich adsorption model had higher regression coefficients as compared to Langmuir and Temkin adsorption isotherms. According to Kabbashi *et al.* (2009), a high or good correlation coefficient is an indication that there was strong adsorption between adsorbate and adsorbent. Low correlation coefficient implies that the adsorption surface is heterogenous in nature (Alswata *et al.*, 2017).

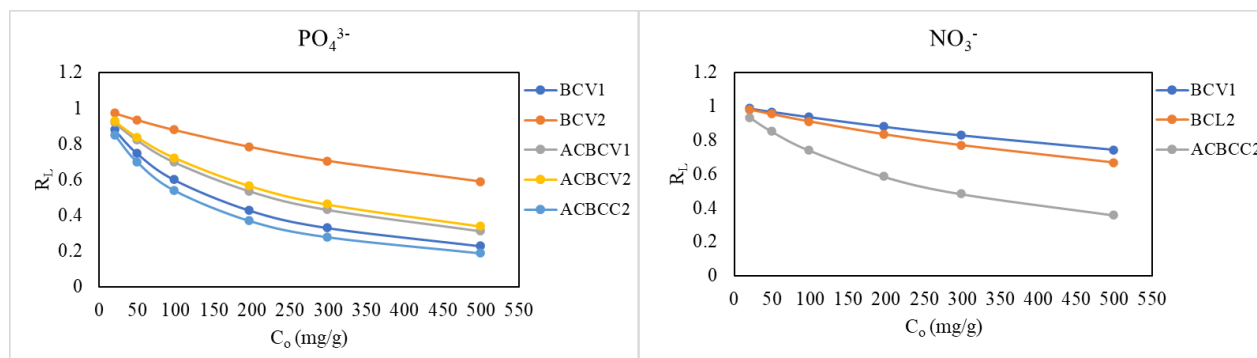


Figure 4.17. Separation factors versus PO_4^{3-} and NO_3^- initial concentrations of ordinary and activated biochars from non-phytoremediation and phytoremediation biomasses of *Cymbopogon citratus*, *Cymbopogon nardus* and *Chrysopogon zizanioides*. BCV1: *Chrysopogon zizanioides* non-phytoremediation biochar, BCV2: *Chrysopogon zizanioides* phytoremediation biochar, BCL2: *Cymbopogon citratus* phytoremediation biochar. ACBCV1: activated *Chrysopogon zizanioides* non-phytoremediation biochar, ACBCV2: activated *Chrysopogon zizanioides* phytoremediation biochar ACBCC2: activated *Cymbopogon nardus* phytoremediation biochar.

Chapter 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Regardless of the grass types, the phytoremediation biomasses have higher heavy metal content (Al, Cu, Fe, Ni, and Mn) than the non-phytoremediation biomasses. The intensities of methyl and methylene surface functional groups decreased from non-phytoremediation biomasses to phytoremediation biomasses. Subsequent biochars indicated higher heavy metal content, ash content, and volatile matter content but had low fixed carbon, pH, and electrical conductivity in the phytoremediation group. The biplot indicated an increase in identified functional groups from non-phytoremediation biochars to phytoremediation biochars except for *Cymbopogon citratus*. Biochars from *Chrysopogon zizanioides* phytoremediation biochars showed low intensities of anatase and dolomite peaks. The structures of biochars from phytoremediation biomasses were less porous as compared to the biochars from non-phytoremediation biomasses.

ZnCl₂-activation did not alter the ordinary surface functional group profiles but increased the ordinary biochar's surface porosity. Crystalline minerals formed in activated biochars were few compared to those of ordinary biochars, and the activation process induced new minerals such as quartz, sphalerite, and chrysolite. Activation of biochars using ZnCl₂ decreased the number of the identified crystalline minerals in ordinary biochars. The activation of ordinary biochars with ZnCl₂ reduced the magnitude of the potential positive charges that can develop and adsorb anions.

Conclusion and Recommendations

Generally, negative adsorption capacities for Al, Cu, Fe, and Ni in AMD solution by phytoremediation biochars were observed as a function of both biochar dosage and adsorption evolution time. For anionic compounds, the activated phytoremediation biochar from *Chrysopogon zizanioides* indicated the highest adsorption capacity of 14.12 mg g^{-1} for PO_4^{3-} ion at a biochar dosage of 0.04 g while activated phytoremediation biochar from *Cymbopogon nardus* retained 20.72 mg g^{-1} of NO_3^- ion. Based on the effect of pH on adsorption, activated non-phytoremediation biochar from *Cymbopogon nardus* showed the maximum adsorption capacities of 38.93 mg g^{-1} and 31.52 mg g^{-1} for PO_4^{3-} and NO_3^- ions, respectively at pH 8. Based on the effect of initial concentration on adsorption, ordinary non-phytoremediation biochar from *Cymbopogon nardus* effectively retained 69.06 mg g^{-1} of PO_4^{3-} ion at the initial concentration of 300 mg l^{-1} while ordinary non-phytoremediation biochar from *Cymbopogon citratus* indicated maximum adsorption of 49.58 mg g^{-1} at an initial concentration of 20 mg l^{-1} .

Langmuir isotherm indicated that the maximum adsorption capacities for PO_4^{3-} that can be reached by BCV1, BCV2, activated BCV1, activated BCV2, and activated BCC2 are 62.99, 72.99, 113.64, 115.70, and 61.38 mg g^{-1} , respectively. BCV1, BCL2 and activated BCC2 can reach maximum adsorption of NO_3^- at 317.71, 294.7 and 99.42 mg g^{-1} , respectively. For NO_3^- adsorption, BCV2, BCC2, BCL1, activated BCV1, BCV2 and BCC1 also were best fitted in the Temkin adsorption equation with maximum possible adsorption capacities at 110.81, 101.39, 255.7, 106.00, 117.71 and 110.19 mg L^{-1} , respectively. The Dubinin-Radushkevich indicated that the maximum PO_4^{3-} adsorption capacity by BCC1 and activated BCC1 is 51.37 and 46.31 mg g^{-1} , respectively. Overall, the biochar from phytoremediation biomasses showed high potential as an adsorbent for the anionic contaminants in wastewater.

5.2 Recommendations

It is recommended that further studies should be conducted concerning the: (1) optimization of the pyrolysis condition of phytoremediation biomasses depending on the type of plant material (species), (2) the kind and concentration of heavy metal contaminants present in the raw biomass and their relationships to the chemical and structural properties of the biochar, and (3) to continuously identify and develop potential uses for biochar products from phytoremediation biomasses. To enhance the heavy metal adsorption performances of phytoremediation biochars, further studies should be carried out to induce net negative surface charges of the phytoremediation matrix. Regarding the disposal of phytoremediation biochars after the adsorption of ionic contaminants, the resultant biochars could be used in cement production since they could reduce thermal conductivity and increase the toughness and strength of cement (Praneeth *et al.*, 2021). Still, a detailed environmental assessment should be conducted to assess the potential environmental threats that biochar's inherent metals could pose. Resultant phytoremediation biochar after adsorption experiments could also be applied in ionic contaminated soils to retain either positive or negative contaminants depending on the charge of the adsorbent but leaching capabilities of ionic contaminants of the adsorbents should be assessed before its application soils. Further studies are needed to elucidate the long-term impact of the disposal of spent biochar in different media.

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