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APPLICATION OF BIOCHAR PRODUCED FROM *PROSOPIS JULIFLORA* PODS FOR THE REMOVAL OF LEAD AND NICKEL FROM ARTIFICIALLY CONTAMINATED SOIL AND ENHANCING TOMATO GROWTH

BY

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ABSTRACT

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Title: Application of Biochar Produced from *Prosopis juliflora* for the Removal of Heavy Metal Pollutants from Contaminated Soil.

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The utilization of biochar is considered an environmentally friendly and cost-effective remediation method. In this regard, the application of biochar produced from *Prosopis juliflora* pods seems to be potentially effective in immobilizing heavy metals and enhancing soil properties and quality. The batch experiment and incubation experiment were conducted with different initial concentrations of Pb (II) and Ni (II), which proved the efficiency of biochar in remediating contaminated aqueous solutions and soil, respectively. The maximum adsorption obtained for Pb (II) was 959.9 mg/g and 270 mg/g, whereas Ni (II) was 381.06 mg/g and 149.95 mg/g, at higher initial concentrations in batch and incubation experiments, respectively. Additionally, a pot experiment was carried out to ensure the efficiency of biochar on the growth of the tomato plant (*Solanum lycopersicum*). Biochar showed a significant impact on tomato plants in terms of growth parameters and yield after the pot experiment. Moreover, Fourier-transform infrared spectroscopy and scanning electron microscopy analyses demonstrated that biochar potentially reduced and remediated contaminated media through several mechanisms, namely, adsorption, precipitation, complexation, ion exchange, and electrostatic interaction. This study concludes that *P. juliflora* biochar potentially improved soil quality and properties and is attributed to enhancing the growth of tomato plants.

DEDICATION

I would like to dedicate this thesis first to my great support circle, my family and friends. Secondly, to the environmental researchers and scientific communities.

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Chapter 1: Introduction

1.1 Research background

The rapid growth of the global population as well as the development associated with increased consumption and production rates of natural resources have put significant pressure on the quality of natural resources, resulting in a variety of consequences that increase pollution in the environment and alter the stability of ecosystems (Gavrilescu, 2021). Industrialization and urbanization activities are considered major contributors to accelerating the production and mobilization of heavy metals in different environmental compartments, such as soil, which is considered the major sink for heavy metals; therefore, they cause one of the major challenges, namely heavy metal pollution (Wuana and Okieimen, 2011; Ali, Khan, and Ilahi, 2019). The serious threats behind the presence of heavy metals in soil affect different aspects globally, such as environmental, economic, and social aspects. This is because heavy metals are characterized as non-biodegradable and persist in the environment with a tendency to bioaccumulate in living organisms (Briffa et al., 2020). Heavy metal pollution is a serious environmental issue that threatens human health because it bioaccumulates gradually through the food chain and causes toxic stress to the abundance of soil microorganisms that determine the quality of soil (Zhao et al., 2019; Hu et al., 2021). Furthermore, the accumulation of heavy metals in the soil will substantially leach into the groundwater, runoff into various water bodies, and bioaccumulate in crops (Wuana and Okieimen, 2011; Jia, Li, and Wang, 2018).

Heavy metals exist naturally through different natural processes such as volcanic eruption and weathering of bedrock (Tchounwou et al., 2012). Furthermore, heavy metals can be classified as essential and nonessential metals for living organisms; essential heavy metals like nickel, zinc, cobalt, iron, and copper are required in trace amounts for different processes, namely, for the growth, development, and metabolic activities of organisms (Raychaudhuri et al., 2021). In contrast, nonessential heavy metals like lead, cadmium, mercury, and aluminum are not required for living organisms, and the presence of these metals in trace amounts poses a toxic impact on the environment (Raychaudhuri et al., 2021). Furthermore, unsustainable and unmanaged land uses for anthropogenic activities result in heavy metal concentrations exceeding the permissible level, which causes soil degradation and has a negative impact on soil quality and food security (Shawai et al., 2017; Hu et al., 2018; Gavrilescu, 2021; González-Henao and Ghneim-Herrera, 2021). The presence of heavy metals in soil depends mainly on the speciation of the metal and its chemical form since heavy metals start to adsorb into the soil and then redistribute into various chemical forms that determine their availability, toxicity level, and mobility (Jaishankar et al., 2014; Li et al., 2022). Lead (Pb) is one of the heavy metals that are commonly found as contaminants in soil and are found to be non-essential for living organisms and highly noxious (Kumar et al., 2020). Additionally, lead exists in the soil as ionic lead, Pb (II), and actively reacts with other chemicals to form different compounds, namely lead phosphate ($Pb_3(PO_4)_2$) and lead carbonate ($PbCO_3$), which were discovered to be insoluble lead compounds (Wuana and Okieimen, 2011). Moreover, lead has been extensively studied to understand its risk effects on human health and the environment (Wuana and Okieimen, 2011; Jaishankar et al., 2014; Kumar et al., 2020). Another heavy metal that affects soil quality is nickel (Ni), which exists in ionic form, namely the nickelous ion Ni (II). It is found in the environment naturally at a low level and is considered essential for organisms. However, a high concentration of Ni tends to pose a serious threat to human health, induce toxic effects in the soil, and damage plants (Amjad et al., 2019; Hassan et al., 2019; Rahi et al., 2021). Table 1 illustrates the international standard values of the threshold and permissible limits of heavy metal content in soil and reflects the risks on the level of human health and the environment (Tóth et al., 2016). In addition, the World Health Organization reported the recommended limits of Pb and Ni in soil, namely, 100 and 50 mg/Kg (Chiroma, Ebewele, and Hymore, 2014).

Table 1. International threshold limit and permissible limit of Pb and Ni in soils (Chiroma et al., 2014; Toth et al., 2016)

Heavy metals	Threshold limit (mg/Kg)	Permissible limit (mg/Kg)	World Health Organization level (mg/Kg)
Pb	60	200 (health risk)	100
Ni	50	100 (ecological risk)	50

If the problem of heavy metal pollution is kept unnoticed, the toxic effect will increase in the environment, which in turn threatens the sustainability of organisms' lives in the long-term. In that case, it is necessary to remediate heavy metals in the contaminated areas to ensure the reduction of their bioavailability and protect the environment and human health (Briffa et al., 2020). Several studies revealed numerous remediation technologies used to treat heavy metal-contaminated soil (Usman et al., 2016; Liu et al., 2018; Li et al., 2019; Da'ana et al., 2021; Raffa et al., 2021; Ahmed et al., 2022). The selection of an effective, appropriate, and acceptable remediation technology depends on several factors related to the contaminated soil, for instance, the site's physicochemical and biological properties, the availability and concentration level of heavy metals, and its characteristics in the environment (Briffa et al., 2020; Heaney; 2020; Elbasiouny et al., 2021). In addition, the technology used must serve the sustainability of the environment through the utilization of low energy, cheap resources, production of less toxic waste, and evaluated as cost-effective.

The treatment of heavy metals contaminated sites can be carried out through different remediation methods which are, biological, chemical, and physical methods; each method has its own capabilities to remove or reduce the concentration of heavy metals and demonstrates different advantages and disadvantages that determine their effectiveness (Khalid et al., 2017; Elbasiouny et al., 2021). The biological methods (bioremediation) occur through the presence or addition of microorganisms that degrade the heavy metals into less harmful forms through their metabolic activities. Additionally, Heavy metal remediation by plants is known as phytoremediation technology (Chibuike, and Obiora, 2014; Hu et al, 2021). While chemical methods represent the addition of chemical substances produced and modified from natural or industrial resources to remove heavy metals by several mechanisms namely ion exchange, precipitation, stabilization, and adsorption (Raffa et al., 2021; Elbasiouny et al., 2021). On the other hand, physical methods include volatilization, landfilling of soil, incineration (thermal treatment), and physical adsorption (Khalid et al., 2017; Da'ana et al., 2021, Elbasiouny et al., 2021). Out of these remediation methods, the application of biochar produced from biological waste has been attracting researcher attention because of its beneficial role in the environment as an adsorbent to remediate and enhance the quality of heavy metal-contaminated soil (Panwar et al., 2019; Yaashikaa et al., 2020; Ali et al., 2021). Applying biochar into contaminated soil could ensure the immobilization of heavy metals through different mechanisms, namely, adsorption, precipitation, ion exchange, and complexation (Cheng et al., 2020). Adsorption is a physical and chemical technique used to remediate contaminated soil since it is represented as a beneficial method because of the low cost applied and the energy consumed through the remediation process (Liang et al., 2021). Furthermore, precipitation reactions occur after the addition of biochar into the soil, which raises the pH and increases the production of precipitated heavy metal ions or reacts with inorganic compounds such as phosphate and carbonate (Liang et al., 2021). Moreover, cation exchange capacity on the surface of biochar enhances the immobilization and adsorption of heavy metals through the reaction of ion exchange of cations such as calcium, magnesium, potassium, and sodium with cationic heavy metals such as lead and nickel (Zhang et al., 2016; Yang et al., 2019). In addition, the surface of biochar is occupied with oxygen-containing functional groups, carboxyl and hydroxyl groups, which were found to be favorable for complexation reactions with heavy metal ions (Bolan et al., 2014; Liang et al., 2021).

Biochar represents carbon material produced from biomass, for instance, plant and animal wastes that are converted through thermochemical processes into biochar under controlled conditions of pressure and temperature rate in a closed system and characterized by the low presence or absence of oxygen (Ahmad et al., 2014; Nartey and Zhao, 2014; Tan et al., 2015; Wang et al., 2020). In different ways, biochar has been used to improve environmental management in different ways, namely: enhancing soil quality and properties (Ahmad et al., 2014; Vijayaraghavan, 2019; Wang et al., 2019; Gomez-Sagasti et al., 2021; Wijitkosum, 2022). In addition, the application of biochar in the agricultural field increases crop yield and prevents the uptake of contaminants by plants (O'Connor et al., 2018). Producing biochar from biodegradable wastes such as agricultural wastes that are composed of a wide range of hemicellulose compounds is determined as a sustainable solution for efficient waste management and reduces its abundance in the environment (Bilias et al., 2021). Therefore, biochar plays a role as an amendment and promotes waste management through the diverting of biological wastes into more effective materials that serve to improve the quality of the environment and ensure its sustainability.

Biochar has unique physical and chemical properties that vary widely depending on the biomass materials that differ in organic and ash composition, and production processes (Guo et al., 2020). Biochar is a porous material characterized by a large surface area, a rough morphological surface, low density, and high porosity because of the dehydration process that occurs during the production process and the emission of different volatile materials (Guo et al., 2020; Amalina et al., 2022). In addition, the biochar surface contains a wide variety of functional groups shown in Figure 1, it is primarily composed of amorphous, aromatic carbon, and oxygen-containing groups, namely, carboxylic, hydroxyl, and lactonic groups, which are controlled by the type of feedstock, temperature, and pH, which therefore affect the cation exchange capacity in biochar (Yaashikaa et al., 2020; Guo et al., 2020). Moreover, the pH value of biochar was found to range from 5 to 12 depending on the water-soluble base cations and organic acids of biochar; where the increase in biochar pH was greatly related to ash mineral content and pyrolysis temperature (Guo et al., 2020).

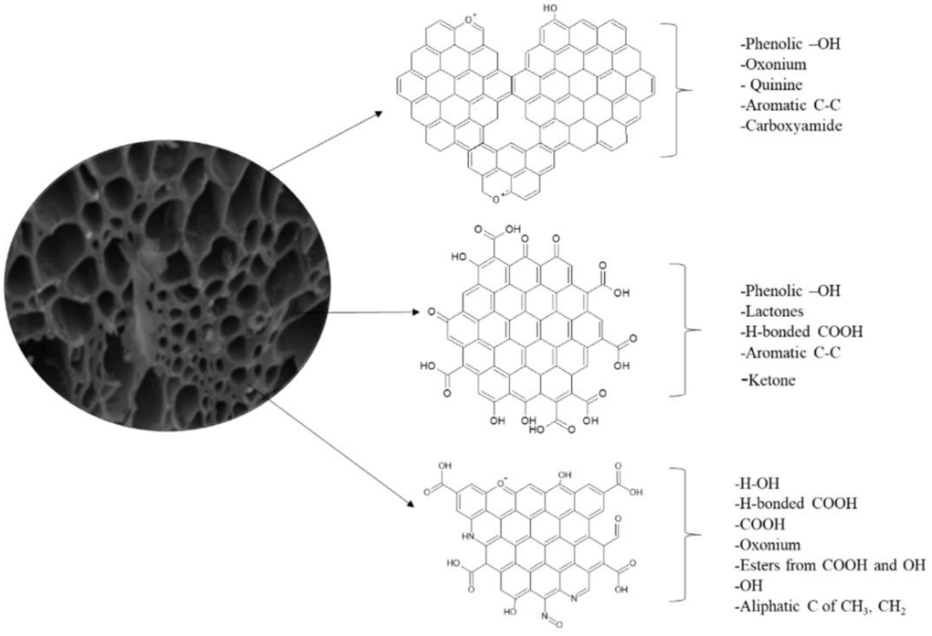

Figure 1. Biochar chemical structure (Nkoh et al., 2021)

The novelty of this project depends on the ability of biochar produced from an invasive plant species in Qatar to remediate polluted soil. This project could help the Ministry of Environment and Climate Change in Qatar to manage and control the distribution and growth of *Prosopis juliflora* in the region and promote the culture of waste management of biological materials. *P. juliflora* possess a negative impact on the environment due to its widespread and rapid distribution and growth in a wide range of environmental conditions such as drought and high temperatures (Patnaik et al., 2017). These impacts affect the growth of native plant species, increasing their mortality because of the ability of *P. juliflora* to colonize land and compete for fundamental resources such as water and nutrients, and it also produces allelochemicals, which reduce biodiversity (Bibi and Abu-Dieyeh, 2016; Patnaik et al., 2017; Usman et al., 2019; Ravhuhali et al., 2021).

1.1.1 Research questions and hypothesis

This project is driven by the following hypotheses that answer different scientific questions that will expand the understanding of the mechanisms of the biochar derived from agricultural waste to remediate heavy metal-contaminated soil and improve the growth of plants.

I. Adsorption of heavy metals by *P. juliflora* biochar is influenced by the initial concentration of heavy metals in water and soil.

II. *P. juliflora* biochar has the potential to adsorb Pb and Ni and the capability of adsorption depends on the physicochemical characterization of the biochar.

III. Addition of biochar to remediate heavy metals in contaminated soil enhances soil quality and promotes tomato growth.

1.1.2 Significance of the study

The current best management practice to avoid the negative impact of *P. juliflora* in the Qatari environment is to utilize it as an adsorbent to remove heavy metals from different media, such as aqueous solutions and soil. Most studies have reported that *P. juliflora* has an excellent ability to grow under the harsh physical and chemical conditions of Qatari soil and climate, making it an appropriate candidate as a low-cost adsorbent. The thermal conversion of *P. juliflora* could promote the removal performance of heavy metals through the enhancement of the physicochemical characteristics of the adsorbent.

In this study, biochar produced from the pods of *P. juliflora* was used for the remediation of lead and nickel-contaminated soil, thereby targeting and utilizing the main contributor to the wide and rapid spread of *P. juliflora*. The analysis presented in this study will convey and serve valuable understanding and knowledge for further future studies to explore, produce, and implement such materials in the fields of soil and agricultural management, which will contribute to the advancement of scientific research that potentially solves heavy metal pollution affecting the environment.

1.1.3 Research objectives

The objectives of this research are as stated below.

I. To study the physicochemical characterization of biochar produced from *Prosopis juliflora* pods.

II. To evaluate the efficiency of the prepared biochar as an adsorbent on the adsorption of lead and nickel from contaminated soil.

III. To investigate the agronomic impact of biochar on the availability of heavy metals in contaminated soil and on tomato growth parameters in a pot experiment.

Chapter 2: Literature Review

2.1 Soil formation and composition

Soil is the foundation of life that is formed in slow processes, namely weathering and deposition of sediment that provides a habitat for organisms, an essential medium for plants to grow, and maintain different environmental sources, for instance, water and air (Khalil et al., 2015; Raju et al., 2017; Kalev and Toor, 2018; Neina, 2019). Soil is considered a heterogeneous dynamic zone, due to the changes that occur by the biological, chemical, and physical processes, as well as the interaction between the soil components namely, organic matters, liquid, and gaseous substances, living organisms (plant and animals), and minerals (Opeyemi et al., 2020).

There are several factors that affect the formation of the soil, namely, climatic change of temperature and precipitation rate, the presence of living organisms, the parent materials and topography of the area, and the formation period (Hartemink et al., 2020). These factors play an important role in soil horizonation and weathering, either chemically, where the rock is broken down into smaller particles due to chemical reactions, such as limestone ($CaCO3$) and water, or physically, where changes in temperature and water cycle break the rock down into different soil sizes, such as sand and silt (Kalev and Toor, 2018; Hartemink et al., 2020).

Furthermore, soil can exist in different textural forms such as clay, silt, and sand. Each texture contains different ranges of organic matter (2–5%), minerals (20–40%), water, and air (10–25%) (Khalil et al., 2015). The physical and chemical properties of soil are highly affected by different factors, namely biological, chemical, physical, and geological factors. These factors can influence the quality and fertility of the soil and affect the distribution of available trace elements and heavy metals (Opeyemi et al., 2020). In addition, determine the characterization of the soil profile and the capacity to support the presence and sustain living organisms (i.e., plants, animals, and humans) (Kalev and Toor, 2018; Hartemink et al., 2020).

2.1.1 Soil properties

2.1.1.1 Physical properties. The physical properties refer to soil structure, soil texture, porosity, soil density, moisture content, and hydraulic conductivity. These properties strongly affect vegetation growth where the soil structure and texture enhance the penetration of water and air, nutrient uptake, and soil fertility (Khalil et al., 2015; Haruna et al., 2020). Natural processes, such as weathering of parent materials, agricultural and industrial activities, and climate change, have a significant impact on soil physical properties; these factors give the soil a distinct combination that varies globally (Callaham and Stanturf, 2021).

Soil structure and morphology. Soil structure is defined as the aggregation and arrangement of soil particles and different sizes of soil pores respectively into specific patterns, which is considered an important factor that influences the growth of plants and controls the water flow and retention, exchanges of gases, presence of organic matter, and nutrient cycles (Almendro-Candel et al., 2018). The soil structure can be classified into different categories, namely (Phogat et al., 2015):

1) Type of soil structure can be illustrated by the shape and arrangement of soil particles, and it is divided into two groups: simple structure and compound structure.
2) Soil structure is classified into five sizes (diameter, mm): very fine soil (1 mm), fine soil (1 mm -2 mm), medium soil (2 mm –5 mm), coarse soil (5 mm –10 mm), and very coarse soil (> 10 mm).
3) The grade of soil structure is determined by the aggregation stability of the soil, which is influenced by several factors such as the content of organic matter, moisture content, and

adsorption of the cations. The stability of soil structure is divided into three categories: weak grade (not stable), moderate grade (stable), and strong grade (highly stable).

The morphology of soil that contains the shape and size of particles and pores could be examined through an analytical technique, namely Scanning Electron Microscopy (SEM), that allows the interaction of high electron energies with the surface of soil grains (Ural, 2021). Extracted images from SEM contribute to a better understanding of soil microstructure and behavior by providing an indication and insight into formation conditions and physical properties of the soil at high resolution and different magnifications (Tang, Shi, and Wang, 2008; Ural, 2021).

Soil texture. The soil composition of different particle sizes, including silt, clay, and sand, with different percentages, describes the soil texture, which affects the soil quality and productivity (Yu et al., 2020). According to the International Society of Soil Science, soil particles can be classified based on their diameter (mm), with clay (0.002 mm), silt (0.02 mm –0.002 mm), and sand ranging from fine sand with 0.2 mm -0.02 mm to coarse sand with 2.0 mm –0.2 mm (Phogat et al., 2015). Each particle size has unique properties, with clay having the highest water and nutrient holding capacity, silt having a medium holding capacity, and sand having a low capacity to hold water and nutrients (Phogat et al., 2015). Different soil textures can be distinguished by measuring the proportion (percentage) of sand, silt, and clay content within the soil media using the textural class triangle illustrated in Figure 2 (Groenendyk et al., 2015). Soil texture can be classified into three major groups, namely, sandy soil (coarse texture), loamy soil (moderately coarse and fine texture), and clayey soil (fine texture) (Phogat et al., 2015; Yu et al., 2020). The sandy soil is characterized by a texture with low water and nutrient-holding capacity, low content of organic matter, and high permeability of water and nutrients (Phogat et al., 2015). However, loamy soil has excellent water and nutrient holding capacity and aeration properties, which are considered favorable properties in agriculture (Phogat et al., 2015). In contrast, clayey soil, also known as heavy textured soil, because it retains more water and becomes highly cohesive when dry with a low aeration rate, and these properties make the clayey soil unfavorable for cultivation (Phogat et al., 2015).

Figure 2. Classes of soil texture according to the particle percentage (Groenendyk et al., 2015)

Soil density. The soil density is measured by dividing the mass of soil quantity by the volume of soil quantity and it can be indicated by measuring the particle density, which is considered the average density of the particles and bulk density to determine the soil compaction and porosity (Martynenko, 2014; Gajda et al., 2020).

Particle density. Particle density (ρ_s) can be determined by the ratio of mass units of solid soil per volume of the soil without measuring the soil pore spaces, and it depends on the soil chemical compositions of mineral and organic matter (Di Giuseppe et al., 2016). The particle density can be calculated using the below equation (Phogat et al., 2015):

$$\rho_s = \frac{M_s}{V_s}$$

Where Ms refers to the dried soil mass in milligrams (mg) or grams (g), and the V_s define as the volume unit of soil solids only and measured in cubic meters (m^3) or cubic centimeters (cm^3).

According to Phogat et al. (2015), the general soil particle density is ranged between 2.6 and 2.7 g/cm^3, and this range includes several soil particle types such as sand, silt, and clay. The particle density of soil can be measured by following the standard method known as the pycnometer method by using either a stoppered bottle with a small soil quantity or a volumetric flask for a large soil quantity (Vennik et al., 2015).

Bulk density. The bulk density (ρ_b) illustrates the amount of available pore space in the soil and the measurement of the dried mass of soil per total volume, and it is measured by the following equation (Ferreira, Borges, and Pires, 2015) :

$$\rho_b = \frac{M_s}{V_t}$$

Where Ms is the mass of the dried soil sample in milligrams (mg) and Vt represents the total volume of dried soil and is expressed in cubic meters (m^3) including pore space.

Bulk density can be measured following several methods that are classified into two groups, namely: 1) direct measurement, such as the core method, cold method, and excavation method; and 2) indirect measurement, for instance, the radiation and regression method (Al-Shammary et al., 2018). The selection of an appropriate method depends on the utilized technology, cost, analysis duration of the measurement, and effectiveness and suitability of the soil used (Al-Shammary et al., 2018). Moreover, bulk density is represented as an indicator of soil porosity, soil compaction, permeability rate, organic matter content, moisture content, and soil texture and structure (Kalev and Toor, 2018; Al-Shammary et al., 2018).

Soil porosity and pore size distribution. The porosity of soil measures the available space and soil volume that does not consist of soil particles and organic matter which water can move through. Soil porosity is classified into three forms, namely, macropores, mesopores, and micropores; the role of each pore is characterized by drainage rate and water availability for plants (Haruna et al., 2020; Callaham and Stanturf, 2021). The pore space of soil is defined as the available space occupied by air (air-filled porosity) and water (water-filled pore space), where the soil that is filled completely with gas is considered as dry soil, compared to the saturated soil that is fully occupied by water (Hao et al., 2008; Phogat et al., 2015). However, the pore space of unsaturated soil is filled with air and water (Phogat et al., 2015).

The ratio of pores space is determined by the soil structure and texture; sandy soil has low porosity with large pores, whereas clayey soil has high porosity with small pores; in this case, soil aeration is highly beneficial in sandy soil due to the large pores (Phogat et al., 2015). In addition, there are several factors affecting soil pore space, including soil texture, cultivation of crops that reduce the pore space and the content of organic matter, and the pores' size, whereas in macropores (sandy soil) the penetration and movement of water are rapid compared to the micropores (clayey soil) (Abdulkadir, 2016). The porosity (η) of soil can be measured by using the following equations (Hao et al., 2008; Abdulkadir, 2016):

- Measuring porosity by volumes

$$\eta = \frac{\text{Pore volume (Vp)}}{\text{Total volume (Vt)}} * 100$$

- Measuring porosity by densities

$$\eta = 1 - \frac{\text{Bulk density (Pb)}}{\text{Particle density (Pd)}}$$

Soil hydrology\ hydrodynamic. Soil is provided with moisture in different ways: either from precipitation from the atmosphere or from the presence of groundwater (Filipović, 2020). Soil moisture content is represented as an important parameter for determining the stability, strength, and aggregation of soil particles; hydrological behavior; crop production and growth; and biological and geological processes (Su, Singh, and Baghini, 2014; Shah et al., 2017). Soil moisture level can be categorized under three levels, which are: wet soil, which describes the stickiness and plasticity of the soil; moist soil, which enhances the particles' coherence and resists crushing of the soil; and dry soil, which represents non-coherent soil because of the absence of moisture. Soil moisture levels also have a different resistance degree that depends on the strength of particle attraction (Abdulkadir, 2016).

Soil moisture content exists in three different forms, namely, gravitational moisture, where the moisture moves rapidly downward because of the gravity force, and the soil porosity, which is considered to be macropores (Su et al., 2014; Nwogwu et al., 2018; Filipović, 2020). In addition, capillary moisture describes the adhesion and cohesion of moisture in the micropores of the soil and plays a role in the interaction between the biological, chemical, and physical properties (Su et al., 2014; Filipović, 2020). Furthermore, hygroscopic moisture is where the moisture is adhered strongly to the surface of the soil particles, forming a thin film around the particles' surface (Su et al., 2014; Nwogwu et al., 2018). The cohesion and adhesion of moisture in the soil depend on several properties such as soil structure, porosity, presence of organic matter and minerals, salinity and temperature rate, and soil depth (Su et al., 2014). On the other hand, several properties of soil are highly dependent on the soil moisture content. For instance, soil strength is inversely related to soil moisture content where the increase in moisture content leads to the reduction of soil strength (Phogat et al., 2015). In addition, soil characterized by high moisture content is coupled with the reduction of bulk density and restricted aeration that lowers the diffusion rate and exchange of gases such as oxygen (Phogat et al., 2015).

The moisture content of the soil can be measured using the following equations (Phogat et al., 2015; Brischke and Wegener, 2019):

- Measuring moisture content by mass (θ_g)

$$\theta_g = \frac{M_w}{M_s} \times 100$$

or

$$\text{MCsoil \%} = \frac{\text{mass of wetted soil (g)} - \text{mass of dried soil (g)}}{\text{mass of dried soil (g)}} \times 100$$

- Measuring moisture content by volume (θ_v)

$$\theta_v = \theta_g \times \rho_b$$

The M_w and M_s represent the mass of water and mass of dried soil respectively and expressed in gram (g), and ρ_b is the bulk density.

Hydraulic conductivity (K) refers to the infiltration of water through soil pore spaces in different ways, namely vertically and horizontally, the flow that is highly influenced by the soil porosity and density, fluid viscosity, and permeability rate (Diminescu, Dumitran, and Vuta, 2019). Hydraulic conductivity can be measured through Darcy's law, which describes the flow of water within porous media, and it can be measured as follows (Phogat and Horn, 2013):

$$J = \frac{Q}{At} = -ki$$

J represents the flow rate of water, Q is the volume discharge of water, A describes the cross-sectional area of flow expressed in square meters (m^2) and t is the unit of time. In addition, K and i consider as the hydraulic conductivity and hydraulic gradient respectively and the negative sign illustrates the flow of water downward.

One of the physical properties that play a role in water movement and enhance soil fertility is water holding capacity (WHC), which represents the ability of soil to retain water required for plant production and growth (Almendro-Candel et al., 2018; Bordoloi et al., 2019). The holding capacity of water depends on the soil texture, availability of organic matter, and particle size; where the soil with a finer texture, high content of organic matter and small particle size that has a large surface area will retain more water (high water holding capacity) (Nwogwu et al., 2018;

Wagner, 2019). According to Brischke and Wegener (2019), WHC can be calculated using the following equation:

$$\text{WHC\%} = \frac{\text{mass of saturated soil (g)} - \text{mass of dried soil (g)}}{\text{mass of dried soil (g)}} \times 100$$

2.1.1.2 Chemical properties. Soil chemistry is mainly formed from the weathering of parent materials, and the chemical properties of soil depend on different substances, namely, organic substances that decompose from plants and animals and inorganic substances such as nutrient elements or metals, where the availability of these substances affects the pH and salinity of soil (Khalil et al., 2015). Each substance plays a role in plant growth, where nutrient availability could promote the growth of plants, the movement of water, and improve the microbial and biological activities in soil. Furthermore, the high amount of organic matter in the soil tends to enhance aggregate stability, which in turn prevents soil erosion and high infiltration rates (Almendro-Candel et al., 2018).

Soil pH. pH is defined as the measurement of the negative logarithm of hydrogen ion (H^+) activity in the soil that illustrates the acidity and alkalinity of the soil; as the H^+ increases, the soil pH also increases and becomes alkaline. However, the soil becomes acidic when the H^+ decreases in the soil (Kalev and Toor, 2018). The pH scale ranges from 0 to 14 and measures the acidity and alkalinity of media; pH 7 refers to neutral; lower than pH 7, the soil becomes acidic; and higher than pH 7, the soil's alkalinity increases (Kalev and Toor, 2018). Soil pH has a strong effect on the soil biogeochemical processes where it influences different processes, for instance, the process of organic biodegradation; mineralization of organic matter; volatilization of ammonia; precipitation of metals and organic matter; exchange capacity of charged elements; and enzymatic activity in soil (Neina, 2019). Furthermore, soil pH influences the adsorption, solubility, and mobility of elements where at low pH the adsorption of elements on the soil surface decreases, and the solubility increases, and these changes depend on the ionic species and its properties (Neina, 2019).

On the other hand, soil pH is controlled by several biogeochemical factors, namely, leaching of positively charged ions (cations), dissolution of carbon dioxide, nitrification and denitrification processes, rhizosphere processes, the addition of organic amendments, humification of organic matter in the soil, and the nature of parent materials; all these factors play a role in producing H^+ (Neina, 2019; Zhang, Wu, and Liu, 2019). According to Oshunsanya (2018), soil pH becomes acidic under wet conditions due to the leaching of weathered materials, but pH becomes neutral or alkaline under dry conditions due to the reduction of weathering processes and material leaching. In addition, there are a number of factors that affect the acidity of the soil. For instance, high precipitation (heavy rainfall), crop roots, the use of fertilizers that lead to the release of hydrogen ions, and oxidative weathering (Oshunsanya, 2018). Compared to the factors that affect soil alkalinity, such as irrigation with bicarbonate dissolved water. Moreover, precipitation and temperature are inversely related to the soil pH, where the weathering rate and flow of minerals and organic matter are influenced by temperature and precipitation, respectively (Zhang et al., 2019).

The regulation of soil pH is found to enhance crop production and growth and promote soil quality. Increases and decreases in pH can be accomplished by adding various natural or synthetic materials. For instance, lime, wood ash, and magnesium oxide are used to increase the soil pH (Kalev and Toor, 2018; Oshunsanya, 2018). In contrast to lowering the soil pH, acidifying fertilizer and organic materials such as ammonium nitrate and peat moss, respectively, (Oshunsanya, 2018).

Soil Cation Exchange Capacity. The presence of water in the soil pore space refers to the aqueous phase that contains different dissolved chemical elements and compounds that exist in different forms, namely, uncharged chemicals and charged chemicals. Charging chemicals are classified either as positively charged ions (cations) or negatively charged ions (anions). Because of their chemical structure with a charged surface and large surface area, soil colloids are considered the finer soil size where chemical interactions occur (Gavrilescu, 2014). Different chemical ions have the ability to be adsorbed on the colloid surface due to the attraction force or exchanged with other ions; these processes depend on the type of charged ion and the size and concentration level of the ions (Raju, Golla, and Vengatampalli, 2017). Exchange capacity is a term that describes the ion sorption ability of the soil surface and the release of ions in the soil solution (exchange ions) (Raju et al., 2017; Mukhopadhyay et al., 2019). The exchange of ions is linked to the charged surface of the soil; if the soil surface is occupied by a negative charge, then it will attract cations (cation exchange capacity), and vice versa, if the surface is dominated by positive charges, then anions will be attracted to the surface (anion exchange capacity) (Raju et al., 2017).

Cation exchange capacity (CEC) illustrates the exchangeable of positively charged ions, for instance, sodium (Na^+), potassium (K^+), and calcium ($Ca2^+$) with other positively charged ions such as H^+ that are adsorbed on the clayey soil surface and organic matter (negatively charged) by the electrostatic force (Aprile and Lorandi, 2012). Studies revealed that CEC considers two major determinants of the quality of soil chemical properties and the sorption capacities of cations onto soil surfaces (Solly et al., 2020). The exchangeable capacity of cations depends on different soil properties, namely, soil texture, pH rate, and organic matter content, where the CEC increases in clay soil that contains a high content of organic matter due to the presence of a high number of negative charges on the surface (Tomasic et al., 2013; Gavrilescu, 2014). In addition, the soil surface charge is strongly influenced by the soil pH and the release of H^+; thereby, a high H^+ concentration tends to lower the soil pH, which in turn neutralizes the surface charge and decreases the CEC (Raju et al., 2017).

Soil Organic Matter. Organic matter is considered as a complex and heterogeneous component found in the soil that is derived from the decomposition of various living organisms, namely plants and animals, by microorganisms at different rates and plays a role in the charge characteristics of soil and enhances the soil quality and fertility (Chenu, Rumpel, and Lehmann, 2015; Jat et al., 2018). According to Curtin et al. (2012), the availability of organic matter in soil supports the presence of nutrients necessary for plant production and microorganism activity, which in turn enhances soil quality. Moreover, organic matter can be classified into plant biomass, which refers to fresh plant waste added to the soil or transformed biomass, where plant detritus is decomposed by microbes (Gleixner, 2013). Soil Organic matter (SOM) mainly consists of different elements that bond together to form different compounds. These elements are carbon, hydrogen, oxygen, nitrogen, and phosphorus. Soil biota assimilates these elements for their reproduction and activity (Gleixner, 2013). For instance, plants are made up of lignocellulose that is composed mainly of C, O, and H bonded together.

Plant litter (dead plant material) represents the main nutrient source in the soil that can be transformed into complex organic matter by microbial transformations and decomposition through the physical fragmentation of complex molecules into simpler compounds (de Godoy Fernandes et al., 2021). Moreover, these simple compounds are taken up by plants through mineralization and absorption processes (de Godoy Fernandes et al., 2021). Furthermore, SOM is composed of energy bonds, which serve as the primary energy source for soil living organisms; it serves as a substrate and product material, providing nutrients and carbon sources for plant growth and microorganisms, respectively; and it stabilizes microorganism enzymatic activities (Riches et al., 2013; Swami et al., 2017; Hoffland et al., 2020).

Organic matter content can be influenced by several soil properties, where the content of organic matter differs with the soil texture; sandy soil tends to have low organic content compared to loamy soil, which is composed of moderate organic matter. However, clayey soil is considered to have high organic matter content (Phogat et al., 2015). On the other hand, organic matter has a diverse effect on a wide range of soil properties that affect the productivity and fertility of the soil. In the case of water holding capacity, a positive correlation exists with organic matter; the increase in organic matter content led to an increase in WHC in certain soil profiles (Murphy, 2015). Furthermore, organic matter has a great impact on the CEC, and it specifically depends on soil pH; when the soil is acidic, the organic matter contributes less to the exchangeable capacity of cations. However, the increase of organic matter in soil tends to increase CEC due to the negatively charged sites of the functional groups that form the organic matter (Krull, Skjemstad, and Baldock, 2004; Murphy, 2015). In addition, the soil aggregate and organic binding systems are greatly ameliorated with the increase of soil organic matter (Krull et al., 2004; Murphy, 2015). Organic matter also influences the biological processes and properties where it is considered a source of energy and nutrients that are stored and released in different environmental compartments and ensure the sustainability of plant production and microorganism activity (Krull et al., 2004).

Soil organic and inorganic matters that chemically form the soil surface and its bonding mechanisms can be obtained through the utilization of an analytical technique, namely Fourier transform infrared (FTIR) spectroscopy, that gives an overall soil chemical profile and is found to be a rapid, nondestructive, and cost-effective quantitative analytical approach (Robinson et al., 2015; Krivoshein et al., 2022; Nath et al., 2022). Transmission spectroscopy is one of the FTIR methods that study the interaction between the soil matter and infrared radiation, first through the passing of the radiation within the soil, then indicating the absorption and transmission of radiation by the soil composition, which appears as a peak in a specific wavenumber spectrum ranging between 400 cm^{-1} and 4000 cm^{-1} that illustrates the fundamental vibrations of organic and inorganic matters (Robinson et al., 2015; Margenot et al., 2016; Ye and Spencer, 2017). Several studies have shown that grinding the soil into fine particle sizes prior to FTIR analysis is critical. According to Stump et al. (2011) and Le Guillou et al. (2015), they investigated that soil particle size less than 2 mm enhances the calibration of FTIR, significantly produces well-defined absorption and sharper peaks and gives an accurate predication of soil organic carbon and soil organic matter in sandy and clayey soils.

Figures 3 and 4 demonstrate the fundamental components of soil reflected in different IR spectra regions (4000 cm^{-1}–400 cm^{-1}) observed in the literature. That encompasses predominantly minerals such as silicates near 1000 cm^{-1}, carbonates at 1400 cm^{-1} or less, and clay minerals that mainly consist of aluminosilicate and OH groups at high wavenumber frequencies ranging from

3700 cm^{-1} to 3500 cm^{-1} (Margenot et al., 2016; Krivoshein et al., 2022). Additionally, low frequencies below 900 cm^{-1} reflect the presence of different carbonates, namely calcite, aragonite, and dolomite (Margenot et al., 2016). On the other hand, soil organic matter (SOM) components lie between 2000 cm^{-1} and 1340 cm^{-1}, which includes the degraded compounds of humic and fulvic acids, carboxylic acid, amide (protein), and ester (Robinson et al., 2015; Krivoshein et al., 2022).

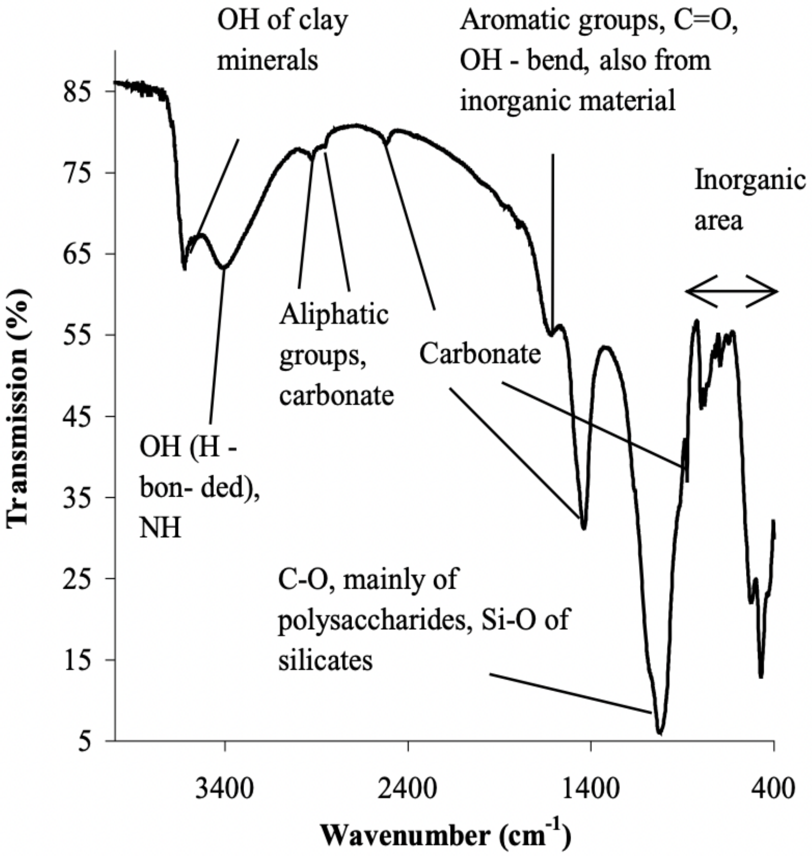

Figure 3. FTIR spectroscopy band interpretations of soil samples (Tatzber et al., 2007).

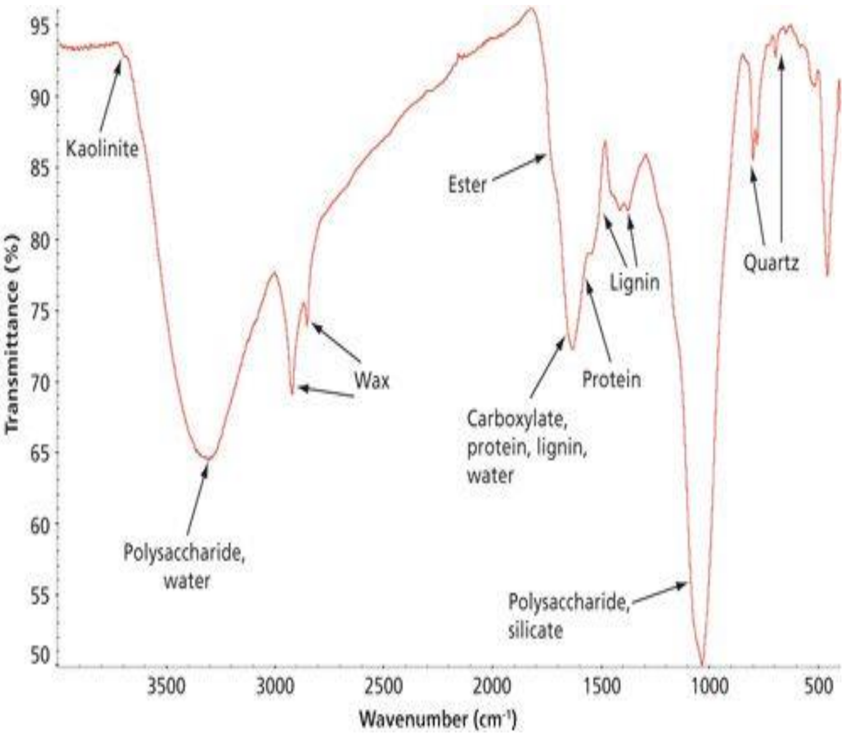

Figure 4. Different infrared (IR) spectra of soil examined in the mid-infrared region (4000 cm^{-1} – 400 cm^{-1}) (Robinson et al., 2015).

2.1.1.3 Biological properties. Soil systems are made up of a diverse and complex community of microorganisms that interact with plants and play various modifying roles in the soil's physicochemical properties (Riches et al., 2013; Kalev and Toor, 2018). Microorganism in the soil (soil fauna) can be classified into 1) bacteria that can provide nutrients through the decomposition of organic matter which improves soil health, 2) fungi that support the function of soil since it considers as a nutrient source for the plant and affect the productivity of soil, and 3) nematodes that enhance the mineralization of nitrogen, decrease phosphate leaching, and improve utilization of substrate (Khalil et al., 2015; Milosevic and Milosevic, 2020). Furthermore, the soil fauna acts as soil engineers because it ameliorates the soil porosity, water holding capacity, and infiltration process through the channels provided by the microbial organisms (McCauley, Jones, and Jacobsen, 2005). These microorganisms play a significant role in soil fertility and quality and improve the development of plants and the mineralization process (Khalil et al., 2015; Milosevic and Milosevic, 2020).

On the other hand, plants highly influence the soil properties through the addition and reduction of soil nutrients and organic matter content, as well as controlling soil temperature and soil water dynamics (Bardgett and Wardle, 2010) Furthermore, the presence of plants and their residues plays an important role in soil structure, as the plant roots encourage soil particles to bind and stick together, and the residues serve as a substrate for microorganisms to decompose organic materials, forming humus that improves soil aggregate (Phogat et al., 2015).

Soil hosts a complex biological activity that influences different ecosystem services, namely the regulating services that include the regulation of biogeochemical cycles, production and growth of crops, and atmospheric trace gases (Lehman et al., 2015). Furthermore, it provides nutrients for primary producers, mitigates and controls natural phenomena such as floods and drought, and bioremediates pollutants (Lehman et al., 2015).

2.1.2 Factors affecting soil properties and quality. Several natural and anthropogenic factors pose a significant impact on soil and result in gradual changes in soil properties and quality. They include agricultural activities, climate change, and the distribution and accumulation of heavy metals (Karmakar et al., 2016; Shabanpour et al., 2020; Briffa et al., 2020).

2.1.2.1 Agricultural activities. Agriculture is considered a major activity that produces pollutants in the environment and degrades soil properties. However, it maintains the level of organic carbon in soil and soil porosity (Almendro-Candel et al., 2018; Shabanpour et al., 2020). The beneficial effects of agricultural residues (organic residues) on soil properties contribute to the enhancement of soil aggregates due to the formation of binding agents, increase the soil organic matter, which provides nutrient elements, and in turn increase the microbial activity (Almendro-Candel et al., 2018).

In contrast, agricultural productivity and activity negatively affect soil health and quality through the application of an inappropriate quantity of fertilizers and pesticides that alter the biogeochemical cycle and the soil hydrodynamics that lead to soil pollution (Trivedi et al., 2016). The application of fertilizers and amendments to improve crop production and soil properties, respectively, resulted in a change in soil reactions and soil pH, resulting in two phenomena: acidification (low pH), which affects nutrient and microorganism availability; and alkalinization (high pH), which reduces infiltration rate, nutrient availability, and hydraulic conductivity (Shahane and Shivay, 2021).

Furthermore, unmanaged crop cultivation affects the soil's chemical properties through the reduction of organic matter. Therefore, nutrient availability will be reduced. Land use changes the ecosystem function, which in turn affects the microbial communities (Rodrigues et al., 2013; Trivedi et al., 2016). According to Chauhan et al. (2012), intensive agricultural practices lead to the degradation of soil properties due to the increase in tillage, which affects the moisture content status and reduces the bulk density of the soil. Furthermore, over-irrigation may result in waterlogging, where the soil becomes saturated with water, affecting soil aeration, soil stability, nutrient leaching, and microorganism availability (Shahane and Shivay, 2021).

2.1.2.2 Climate change. Soil properties are highly affected by climate change scenarios, namely high emissions of carbon dioxide (CO_2) and temperature, where this phenomenon influences the microbiological activities, the presence of organic matter and nutrients, cation exchange capacity, soil aggregate stability, water infiltration rate, and reduces the production and growth of plants (Karmakar et al., 2016; Jat et al., 2018). Temperature and precipitation rate both have a significant impact on soil properties; at high soil temperatures, organic matter decomposition is accelerated, microbial activities are accelerated, nutrients and minerals weather, and the nitrification rate is accelerated (Jat et al., 2018). Climate change alters the precipitation rate due to high temperatures and decreased precipitation; this controls moisture content in the soil, and increases the evaporation rate, but decreases water infiltration and storage (Karmakar et al., 2016). Additionally, according to Zhang et al. (2019), the change in climate affects the chemical processes in the soil, which in turn influences the soil pH. Whereas the soil in an arid climate tends to have a high pH (alkaline), in a humid climate the pH decreases, and the soil becomes more acidic.

Furthermore, the loss of organic matter due to climate change has resulted in decreased water holding capacity and soil fertility, while also increasing bulk density, water infiltration rate, and erosion risk (Karmakar et al., 2016). Moreover, Allen Singh and Dalal (2011) stated that the consequences of climate change influence soil porosity and root development, which in turn affect the biological activities of microorganisms.

2.1.2.3 Heavy metals pollution. Heavy metals are present naturally in the environment or through anthropogenic activities that accelerate their availability and, in turn, cause a harmful impact on the environment (Wuana and Okieimen, 2011; Chibuike and Obiora, 2014). The accumulation of heavy metals in soil results from waste discharge, atmospheric deposition, automobile emissions, and the application of fertilizers, pesticides, and wastewater. All these activities threaten soil productivity and properties (Nuralykyzy et al., 2021). Different factors affect the availability and distribution of heavy metals in soil, namely, soil composition and properties, metal speciation, weathering rate, and climatic conditions (Arunakumara, Walpola, and Yoon, 2013; Ali et al., 2019). Heavy metals are characterized as non-degradable metals; therefore, they accumulate in soil and cause toxic effects that influence microbial activity. This affects the circulation of soil nutrients, reduces soil fertility, and changes the ecosystem function of the soil (Hu et al., 2021; Nuralykyzy et al., 2021). Heavy metal distribution, pollutant impact, and remediation methods will be discussed further in section 2.2.

2.2 Heavy metals

2.2.1 Origin and distribution of heavy metals. Heavy metals are metallic elements that have a high density and atomic weight, which can be classified into two groups namely, macronutrients such as copper (Cu) and magnesium (Mg), and micronutrients which are considered to be essential for living organisms, for example, nickel (Ni), iron (Fe), and zinc (Zn) (Kinuthia et al., 2020; Raffa et al., 2021). The high concentration of these micronutrients could cause a toxic effect on the environment (Shahzad et al., 2018; Raffa et al., 2021). However, there are different heavy metals that are non-essential and play a role as contaminating agents in the environment at low concentrations and cause harmful effects, such as lead (Pb), arsenic (As), and mercury (Hg) (Briffa et al., 2020).

Heavy metals in the environment are derived from natural or anthropogenic sources. For example, the primary source of heavy metals in soil is derived from parent materials that originated in the earth's crust, where the rocks, namely magmatic and metamorphic rocks, are rich in diverse concentrations of copper, cadmium, lead, nickel, and manganese (Bradl, 2005). These heavy metals spread in several environmental compartments such as soil and water in different phases, namely, solid, liquid, or gaseous phases (Vareda et al., 2016; Masindi and Muedi, 2018). In addition, heavy metals reach the soil through natural processes, namely, erosion, weathering, volcanic eruption, leaching, terrestrial changes, and biogenic (Cimboláková et al., 2020). However, some anthropogenic activities accelerate the presence of heavy metals in the environment; these unmanaged activities include mining, fossil fuel combustion, discharge of municipal solid wastes, wastewater effluents, and application of fertilizer and pesticides on agricultural land, which are considered to be the prime causes of environmental pollution with heavy metals (Li et al., 2019; Briffa et al., 2020). Anthropogenic activities play a significant role in the alteration of the biological, chemical, and physical nature of the environment (Cimboláková et al., 2020).

The transportation of heavy metals depends on several environmental factors, namely, the composition of soil and the physical and chemical properties of the pollutants and contaminated sites such as temperature, pH, vapor pressure, partition coefficient, circulation pattern of air, thermodynamic stability, and polarity (Briffa et al., 2020). It is estimated that five million square kilometers (Km^2) of soil have been contaminated by heavy metals, primarily in developed countries such as China and the United States, where 810,000 Km^2 and 6000 Km^2 have been contaminated, respectively (Raffa et al., 2021). The toxic concentration of these contaminants depends on the environmental conditions and the physicochemical properties of the soil, where the distribution of heavy metals is increased in topsoil and reduced with depth (Raffa et al., 2021).

2.2.2 Properties of heavy metals. Heavy metals in the environment are considered non-biodegradable metals that cannot be broken down and have complex interactions, namely chemically and biologically in the environment (Violante et al., 2010; Briffa et al., 2020). Heavy metals have densities greater than 5 g/cm^3 and are classified into two groups: anionic metals (negatively charged) such as arsenic and cationic metals (positively charged) such as mercury, lead, and nickel (Olaniran et al., 2013; Ali, Khan, and Ilahi, 2019). Therefore, heavy metals tend to bind covalently with organic compounds and nonmetallic elements that cannot be broken down and degrade naturally, which in turn causes toxic effects in the environment, for instance, the binding of lead with sulfhydryl groups (Briffa et al., 2020). Furthermore, heavy metals can form lipophilic compounds and cause high toxicity effects that damage human health, animals, and plants, an example of these compounds is tributyltin oxide (Briffa et al., 2020). Moreover, heavy metals exist in different physical or chemical forms, for instance, soil-adsorbed metals, soluble metals, and ionic solute metals (Kalis, 2006). The chemical speciation of heavy metals play a role in their mobility and availability in the environment, which depends on various physicochemical properties, namely, pH, the concentration of organic and inorganic molecules, and nutrient availability (Violante et al., 2010; Ahn et al., 2020). Additionally, redox reactions are considered an important factor that affects the mobilization of heavy metals. For instance, the ability of certain microorganisms to reduce different heavy metals, thereby restricting their distribution and toxicity (Violante et al., 2010).

2.2.2.1 Behavior of heavy metals in soil. Soil is a multicomponent system that covers three phases: solid, gaseous, and liquid phases, where metals can be partitioned within these phases. Heavy metal availability, fractionation, and speciation in the solid and solution phases in the soil can be classified into different chemical and physical mechanisms that can exist in various forms based on the soil diversity, complexity, physicochemical properties, and compositions (Li et al., 2022). Bonding mechanisms with inorganic and organic components considered as chemical mechanisms include bonding with aluminosilicate, carbonate, iron oxide, and organic matter (Li et al., 2022). Furthermore, soil colloids' surfaces contain a net of negative charge that can adsorb and retain cationic heavy metals (positively charged), and this refers to cation exchange capacity (CEC) and can be measured either in cmol/Kg or meqv/100 g of soil (Kachova, 2015). According to Orhue and Frank (2011), soil organic matter is composed of various oxygen-containing functional groups that serve as exchange sites for heavy metals, and the increase in SOM percentage leads to an increase in CEC, which in turn enhances the removal of cationic heavy metals.

On the other hand, physical mechanisms depend on soil particle size and electrostatic interaction. According to Manceau, Marcus, and Tamura (2002), the finest particles are considered the most reactive portion of soil that is composed of colloids, defined as the smaller size fractions of clay and organic matter in soil and characterized by large surface area. In addition, it relied on the outer-sphere surface charge of soil where metals are retained by electrostatic interaction.

Adsorption of heavy metals by inorganic compounds. Inorganic matter in soil is composed mainly of mineral components that include variations of silicate minerals and amorphous and crystalline oxides that affect the mobility of heavy metals within the soil (Li et al., 2022). Furthermore, soil chemical composition also contains kaolinite (a clay mineral) with a structural formula of $Al_2Si_2O_5OH_4$ that has a different adsorption capacity for heavy metals (Li et al., 2022). Additionally, aluminosilicate minerals, which encompass oxides of aluminum and silicon, form three-dimensional structures with tetrahedra linked with oxygen and are characterized by negatively charged surfaces that attract heavy metals with positive charges (Murtić et al., 2020; Li et al., 2022). Moreover, iron oxide (Fe_2O_3) is considered to be a secondary mineral in soil that is characterized by a large surface area and a high abundance of surface hydroxyl groups, which in turn gives it the ability to adsorb and immobilize different heavy metals through retention mechanisms (Shi et al., 2021; Li et al., 2022). The retention mechanisms involve complexation, precipitation, and structural incorporation by diffusion (Shi et al., 2021).

Adsorption of heavy metals by organic compounds. Organic matter in soil contains different functional groups, namely carboxyl, hydroxyl, and amine, that play a significant role in stabilizing and reducing heavy metal bioavailability through several complexation reactions (Li et al., 2022). In addition, it contains dissolved organic matter (DOM) that is composed of a variety of functional groups. An investigation study done by Liu et al. (2021) found that DOM composes of different groups namely hydroxyl, carboxyl, polysaccharide, amino, and fatty acid groups that potentially participate in the adsorption of heavy metals. Furthermore, particulate organic matter (POM) acts as a carrier of heavy metals due to its small size and the abundance of available sites on its surface for adsorption (Zhou et al., 2018).

2.2.3 Environmental pollution. The acceleration of industrial and urban development led to the high exploitation rate of natural resources, which in turn exacerbates the negative impact of environmental pollution that can cause risks to all spheres, for instance, the lithosphere, biosphere, and hydrosphere (Briffa et al., 2020). The pollutants added to the environment are classified into two groups, namely, biodegradable pollutants that decompose by microorganisms and remain for a short time in the environment or nonbiodegradable pollutants that are determined to be persistent in the environment (Babalola, 2018). In addition, these groups consist of organic pollutants, which refer to compounds with carbon bonds, or inorganic pollutants that include heavy metals, nitrogen, and phosphorus (Heaney, 2020). Environmental pollution can be categorized into different groups, for instance, soil pollution and water pollution.

2.2.3.1 Soil pollution. Soil pollution is considered to be a worldwide problem that is caused by agricultural activities that contribute to soil contamination with heavy metals through wastewater irrigation, the use of pesticides and fertilizers, and livestock manure (Trivedi et al., 2016; Li and Xing, 2020). In addition to industrial activities such as coal combustion and municipal waste dumping, which endanger food security and human health. (Zwolak et al., 2019). Heavy metals can be absorbed by crops that tend to be edible for animals and humans, which in turn leads to the bioaccumulation of heavy metals gradually along the food chain (Briffa et al., 2020).

Moreover, it reduces the biodiversity of microorganisms, which in turn negatively affects the biogeochemical cycles and soil fertility (Babalola, 2018). Heavy metals alter the cellular metabolic pathways in plants and change their physiological, biological, and chemical mechanisms (Ali et al., 2021). The impact of heavy metals extends to affecting root proliferation and elongation in addition to the transpiration rate, which reduces the uptake of water and nutrients and lowers the osmotic potential and photosynthetic rate (Rucinska-Sobkowiak, 2016). Furthermore, the presence of heavy metals in soil reduces the availability of several essential nutrients due to the competition for adsorption and absorption in roots (Ali et al., 2021).

2.2.3.2 Water pollution. Water is a very precious resource that has been negatively affected by anthropogenic activities. The rapid increase in the global population and the high consumption rate of water by different sectors, namely agricultural, domestic, and industrial sectors, has resulted in the generation of waste that carries a high concentration of contaminants (Kumar et al., 2019). Heavy metals reach water bodies through runoff from contaminated soil or mining areas, discharge of industrial or domestic waste, and disposal of untreated sewage (Babalola, 2018; Briffa et al., 2020). The solubility of metals depends mainly on the pH of the water, where the presence of heavy metals in bodies of water causes a reduction in pH, which in turn decreases the solubility of metals and increases precipitation downward (Briffa et al., 2020). The wastewater might contain heavy metals that can be accumulated in the soil, which represents the major sink for heavy metals due to its retention capacities. This affects the growth of the plant and reduces the crop yield, which in turn leads to food insecurity (Chibuike and Obiora, 2014; Masindi and Muedi, 2018).

2.2.4 Heavy metals toxicity in the environment. Heavy metals are considered toxic to the environment and humans, even at low concentrations. Some examples of heavy metals that exist in the environment and pose significant threats include arsenic, boron, cadmium, chromium, copper, lead, mercury, nickel, and zinc (Vardhan et al., 2019). Some of these heavy metals could be beneficial for the growth of plants in low concentrations, but they become harmful/toxic when they exceed the permissible limits, such as nickel and zinc (Briffa et al., 2020). The contamination of water and soil with heavy metals discharged from different sources such as smelting, mining, wastewater irrigation, pesticides, and petroleum refining poses a significant threat to living organisms because of their ability to bioaccumulate in the food chain where they cause physiological, functional, and biological complications (Babalola, 2018; Shakya and Agarwal, 2019; Briffa et al., 2020).

Several research and studies have demonstrated the associated risks of heavy metal exposure, where the toxicity and threat of heavy metals extend to impacting negatively all the environmental spheres, namely, the hydrosphere, atmosphere, lithosphere, and biosphere (Briffa et al., 2020; Heaney, 2020). For example, heavy metal exposure can occur via several routes, including inhalation, dermal contact, and ingestion; humans exposed to high concentrations of heavy metals are highly susceptible to neurotoxicity, carcinogenic disease, cell damage, and enzymatic activity inhibition (Briffa et al., 2020; Heaney, 2020). The effect of heavy metals on the environment depends mainly on the concentration of heavy metals, ion species, and free radicals' generation (Tchounwou et al., 2012). Among heavy metals, lead and nickel are considered global matters of concern due to their negative impact on the environment, where they specifically threaten soil quality and water security. According to the World Health Organization (WHO), the limited concentration of Pb and Ni in soil should not exceed 0.1 mg/kg and 0.05 mg/kg, respectively (Raffa et al., 2021).

2.2.4.1 Lead (Pb). Lead is found naturally in the earth's crust with a concentration ranging from 2 to 200 mg/kg, and it is characterized as a gray metal with a density of 11.3 g/cm^3. It belongs to group 14 of the periodic table, and it is considered to be a non-essential element to the environment, especially for living organisms (Tchounwou et al., 2012; Heaney, 2020). This heavy metal is derived from mining activity, coal burning, the combustion of leaded gasoline, and industrial and municipal wastes (Vareda et al., 2016; Li et al., 2019). Lead has been used in different areas, namely producing insecticides, automobile batteries, sports equipment, and lead piping (Briffa et al., 2020).

Lead can bind to different biological molecules that leads to changes in their functions and damage their activities through various mechanisms, also altering the mobility of essential nutrients such as calcium (Tchounwou et al., 2012). Lead exposure causes either acute toxicity or chronic toxicity, and high exposure to lead could cause adverse impacts on humans, including damage to the circulatory, immune, and nervous systems; bone resorption; and high blood pressure (Briffa et al., 2020). Moreover, Lead has been identified as possibly carcinogenic by the International Agency for Research on Cancer (IARC). Pb-contaminated soil affects agricultural fields, where it accumulates in plants due to oxidation and weathering (Igalavithana et al., 2019; Ali et al., 2021).

2.2.4.2 Nickel (Ni). Nickle is considered a heavy metal at high concentration with a density of 8.9 g/cm^3, an atomic number of 28, and belongs to group 10 of the periodic tables (Iyaka, 2011; Kumar et al., 2019). Nickel is one of the essential elements that promote plant growth, with an average concentration in soil ranging from 0.05 to 10 ppm (low concentration) and being present as $[Ni(H_2O)_6]^{2+}$; however, at high concentrations, it becomes harmful to plants and soil (Hassan et al., 2019). The concentration of Ni differs and depends on the soil components and water's physicochemical properties; the natural concentration in soil is lower than 100 ppm and in water 0.005 ppm (Shahzad et al., 2018; Hassan et al., 2019). The associated risks belong to the excess concentration of nickel in soil, which results in lowering the germination rate, and the uptake of nutrients, and also reducing the photosynthesis and transpiration rate (Hassan et al., 2019). Furthermore, nickel is a nonbiodegradable metal in the aqueous environment and a high concentration exists through the leaching of rocks and discharge of waste containing nickel (Kumar et al., 2019).

Nickel is mainly obtained from volcanic processes, industrial effluents, and automobile factories (Francy et al., 2020). In addition, it is commonly formed from the burning of fossil fuels and metal processing factories that exist at low pH. However, it precipitates at high pH and is immobilized once it adsorbs into soil particles (Vareda et al., 2016). Nickel has a negative impact on human health because it causes problems in the respiratory system and heart diseases since it is absorbed as a lipophilic compound. In addition, people who are exposed to nickel in the industry are more likely to get cancer because nickel has the ability to generate free radicals (Briffa et al., 2020).

2.2.5 Remediation technologies. Heavy metals tend to be persistent in the environment and cause hazardous effects. Therefore, proper remediation of contaminated areas with heavy metals is necessary to lower their bioavailability and protect the environment and human health (Briffa et al., 2020). There are several technologies used to treat contaminated soil, which is divided into two categories: in situ remediation, which occurs in the original location; and ex-situ remediation, which occurs outside the original location (Li et al., 2019). The selection of appropriate technology depends on several factors, including site characteristics, concentration level, and type of contaminants (Briffa et al., 2020; Heaney, 2020). In addition, remediation technologies could be carried out through three different methods, namely, biological, chemical, and physical methods, and each method demonstrates several advantages and disadvantages that determine their effectiveness and applicability (Babalola, 2018; Kumar et al., 2019; Guo, Song, and Tian, 2020; Heaney, 2020). The role of these methods is to completely remove the contaminants or transform them into less harmful forms through different mechanisms (Raffa et al., 2021). A comparison of different contaminated soil remediation methods are displayed in Table 2

2.2.5.1 Physical remediation. Physical remediation includes the replacement of soil with uncontaminated soil through landfilling, or surface capping, and thermal treatment through heating the soil surface with high vapor pressure (Babalola, 2018; Raffa et al., 2021). These remediation methods are considered to be highly effective for removing heavy metals and simple. However, they are expensive and change the physical characteristics of soil, for instance, soil texture and particle size distribution, which in turn affect soil fertility (Raffa et al., 2021).

Thermal treatment is based on the application of high temperatures ranging between 200 and 700^{o}C to reduce the mobility and concentration of heavy metals through the formation of volatile materials (Babalola, 2018). In this method, the volatile contaminants are desorbed from soil particles and collected by a carrier gas. Wang et al. (2018) used thermal treatment to lower the mobility and bioavailability of zinc and copper. The results demonstrated that the concentration of heavy metals decreased with the increase in temperature. Thermal treatment is considered to be effective for reducing the availability of heavy metals. However, it requires a high cost for the operations and control systems for the emitted gases that can damage the environment (Raffa et al., 2021)

2.2.5.2 Biological remediation. Bioremediation is the use of microbes or plants to treat contaminated areas. This includes several processes, namely, biodegradation by microorganisms, biological stabilization, phytoremediation, and bioaugmentation (Babalola, 2018; Raffa et al., 2021). Organic contaminants can be easily degraded by microorganisms. However, heavy metals are removed through phytoremediation (Heaney; 2020). Furthermore, microorganisms with specific activity and strain can reduce heavy metals through detoxification processes, and this could reduce the redox state, mobility, and toxicity rate of heavy metals or improve the degradation of heavy metals and soil fertility (Violante et al., 2010; Raffa et al., 2021).

Microbial remediation refers to the ability of microorganisms to remove heavy metals and reduce their mobility and bioavailability through oxidation and reduction reactions; biosorption where heavy metals are bound onto bioadsorbent surfaces; and biological leaching through the formation of biosurfactants (Zabochnicka-Swiatek and Krzywonos, 2014; Yang et al., 2018; Raffa et al., 2021). Using microorganisms to remediate contaminated environments tends to be cost-effective and eco-friendly. However, the main drawback of this method is a long time required to remove heavy metals and environmental conditions that affect microbial activity and metabolism (Raffa et al., 2021).

Phytoremediation refers to a method that uses plants to accumulate, immobilize, and remove contaminants through different strategies, namely phytoextraction, phytodegradation, and phytostabilization (Babalola, 2018). The main mechanism of this method is to sequester heavy metals by the plant’s roots, transfer them into a less toxic form, and through biosorption onto roots or shoots (Ancona et al., 2020). Some of the phytoremediators can be classified as hyperaccumulator plants that can accumulate high percentage of heavy metals ranging between 1000 mg/kg and 10,000 mg/kg (Nwaichi and Dhankher, 2016). Furthermore, this method is regarded as a low-cost technology. However, its limitations include plant selection for remediation and the time required to remove and treat the contaminated area (Babalola, 2018; Heaney, 2020).

2.2.5.3 Chemical remediation. Chemical remediation is the use of chemical reagents or amendments to remove heavy metals from contaminated soil through different mechanisms, namely ion exchange, redox reaction, precipitation, soil washing, stabilization/solidification, and adsorption, that effectively reduce the presence of organic and inorganic contaminants (Babalola, 2018; Raffa et al., 2021). Precipitation refers to the addition of precipitating agents that react with heavy metals and transfer them into insoluble solid particles. The excess addition of chemical agents could cause environmental pollution (Kumar et al., 2019).

Soil washing is a process that allows the leaching of heavy metals through the addition and mixing of reagents and extractants such as chelating agents, surfactants, and humic substances with soil that has been dug-out and extracted from contaminated areas (Babalola, 2018). This method occurs rapidly when the pollutants are transformed from the solid phase to the liquid phase, which is easily separated from the leachate by different physical and chemical processes, namely, desorption and ion exchange (Babalola, 2018). Guo et al. (2016) added different chelators to contaminated soil with multiple heavy metals and the result showed an improvement in heavy metal washing. Soil washing has the potential to introduce new contaminants into the environment (secondary pollution), as well as change and damage soil structure and function (Raffa et al., 2021).

Another chemical process is stabilization/solidification. This technique depends first on stabilizing the contaminants in soil and reducing their mobility through the addition of chemical agents; and secondly, on using solidifying agents to form a block to avoid the leaching of heavy metals (Raffa et al., 2021). Chemical stabilizers are materials used to improve the precipitation, immobilization, and adsorption of heavy metals; for instance, zeolite, activated carbon, and biochar. The selection of an appropriate stabilizer is important to avoid secondary pollution; using materials that are produced from natural waste is considered cost-effective and environmentally friendly. Among the amendments used to remediate the contaminated soil with heavy metals, biochar has received wide and great attention as an effective adsorbent in removing and reducing the bioavailability of heavy metals through different physical and chemical mechanisms, for instance, adsorption (Ali et al., 2021). Biochar is originally prepared from biological materials through thermochemical processes and has been found to be beneficial for enhancing soil fertility and quality (Ali et al., 2021).

Among all the remediation technologies used to remove heavy metals, adsorption has received great attention and has been shown to be an effective method because it is considered an environmentally friendly technique and one of the low-cost technologies (Babalola, 2018; Shahmirzadi et al., 2018). This promising process can remove contaminants at low concentrations effectively, either physically or chemically (Babalola, 2018). Many types of adsorbents have been used to remove heavy metals, for example, natural materials or modified materials from several sources, such as agricultural waste and industrial waste (Shahmirzadi et al., 2018; Gong et al., 2020).

Adsorption is a technique used to remove and reduce contaminants, namely dyes, heavy metals, and organic and inorganic contaminants, from the soil. The adsorption process is defined as a phase transfer method that allows substances (adsorbates) in the fluid phase to attach to a solid surface (adsorbent) (Shahmirzadi et al., 2018). The process relied mainly on the type, nature, and physicochemical characterization of the adsorbent; various types of adsorbent materials play a role in the process, and it is categorized into two groups, namely natural adsorbent, and engineered adsorbent (Worch, 2012; Shahmirzadi et al., 2018). Natural adsorbents are derived from agricultural, biological, or industrial waste. However, engineered adsorbents can be produced by different physical and chemical techniques to form char, activated carbon, or carbon nanotubes (Shahmirzadi et al., 2018). In addition, the availability of the adsorbents, the preparation and production cost, and adsorptive properties all play a role as factors in the appropriate selection of adsorbents for the adsorption process (Aljeboree et al., 2017). The engineered adsorbent was found to be expensive compared to the natural adsorbent. However, it has the highest adsorption capacity because of its physical properties, namely its large surface area (Worch, 2012). Among all types of adsorbents, biochar is shown to adsorb pollutants effectively and has been vas used as a low-cost adsorbent to remediate contaminated soil (Babalola, 2018).

The adsorption process is influenced by several factors that affect the removal capacity of the pollutants; the factors are classified into physical parameters such as pH, temperature, adsorbents' particle size, residence time, and adsorbate concentration (Tran et al., 2016). The surface charge of adsorbent changes with pH, becoming positively charged in acidic conditions and negatively charged in basic conditions (Anah and Astrini, 2017). Furthermore, the effect of temperature affects the adsorption capacity; as the temperature increases with the increase of the adsorption removal capacity, this indicates that the process is endothermic (Takassi et al., 2015). Conversely, the process becomes exothermic if the adsorption capacity decreases with the increase in temperature (Ponnusamy et al., 2014). Also, the efficiency of the adsorption capacity can be measured by the particle size of the adsorbent; if the particle size is small, this indicates that the surface area and the porosity are high, which increases the removal capacity of the adsorbate (Ikenyiri and Ukpaka, 2016). Another factor affecting the adsorption process is the adsorbate concentration; as it increases, the efficiency of adsorption capacity reduces because of the less availability of active sites on the adsorbent surface (Panda et al., 2017).

Different studies must be conducted in order to understand the adsorption mechanisms, namely, studying the adsorption isotherm, adsorption kinetics, and thermodynamics. This determines the interaction between the adsorbent and adsorbate, the nature of the process, and the rate of adsorption (Vareda et al., 2016; Tran et al., 2016; Aljeboree et al., 2017). Adsorption isotherms study the relationship between the adsorbate concentration adsorbed on the adsorbent and the remaining concentration after the adsorption process reaches its equilibrium (Lima et al., 2015). Several isotherms with different examinations can be used, such as Langmuir, Freundlich, and Temkin, to understand the interaction between adsorbate and adsorbent (Tran et al., 2016). In addition, the study of adsorption kinetics allows us to understand the adsorption diffusion rates where the process begins with the transfer of adsorbate from the fluid phase to the external surface of the adsorbent, then moves to the internal surface, and ends up with the full interaction (Aljeboree et al., 2017). Furthermore, the thermodynamic study illustrates the nature of the adsorption process using different parameters, namely, Gibbs free energy, enthalpy, and entropy. The change of these parameters after the adsorption process gives information on whether the process is chemisorption or physisorption, endothermic or exothermic, and spontaneous or nonspontaneous (Worch, 2012; Aljeboree et al., 2017).

There is a great interest in research for the remediation of contaminated soil with heavy metals by using low-cost adsorbents produced from agricultural by-products (Babalola, 2018). Researchers have been focused on converting biological materials into biochar to treat and remediate polluted soil because it has shown an effective removal and adsorption of various heavy metals such as mercury, arsenic, cadmium, lead, and nickel (Lee et al., 2013; Liu et al., 2019; Cheng et al., 2020; Pineda-Puglla et al., 2020).

Table 2. Comparison of different contaminated soil remediation methods (Khalid et al., 2017).

Technique	Process	Advantages	Limitations	Acceptance
		Biological remediation		
Phytoremediation	Use plant that tolerate harsh conditions, and able to accumulate contaminants	- Cost-effective - Effective in remediating contaminated soil	- Hard to control and manage the release of contaminants. - Long time treatment - Require of specific site - Food chain contamination	Low to medium
Microbial remediation	Use microorganisms to immobilize, biodegrade and enhance soil fertility and quality	- Improve the growth of plant - Prevent the translocation of contaminants in plant	- Require specific microorganisms - Dependable on soil and contaminants properties	Very high
		Chemical remediation		
Soil washing	Use different reagents and extractants that can leach contaminants from soil and form stable complexes	- Cost-effective - Removes contaminants completely.	- Extractant might have negative impact in environment - Depends on soil and contaminants properties	Medium to high
Immobilization process	Use of adsorbent from organic and inorganic materials to immobilize and reduce the bioavailability of contaminants	- Low-cost - Quick and easy in application and efficient in immobilizing wide variety of contaminants	- Temporary - Require permanent monitoring of contaminated site	High

Technique	Process	Advantages	Limitations	Acceptance
Physical Remediation				
Thermal Treatment	Application of high temperature at the contaminated site and converts contaminants into vitreous materials	- Easy application - Effective to remove variety of contaminants	- Costly due to the application - Requirement of high energy	Very low
Soil replacement	Replace contaminated soil with uncontaminated soil	- Isolate contaminants effectively form soil - Efficient in highly contaminated soil	- Expensive for excavation, transportation, and disposal operation - High labor work - Suitable for small area - Loss of soil fertility	Very low

2.3 Biochar as a soil remediator

One of the effective and practical ways to manage and decrease the pollution released from biological material wastes is to convert them into useful products such as biochar (Vijayaraghavan, 2019). A growing interest in biochar research and application has attracted researchers' attention due to its benefits for the environment as an adsorbent (Panwar et al., 2019). Biochar is a carbon material prepared and produced from biomass that is converted through thermochemical processes, for instance, gasification, torrefaction, and pyrolysis, into biochar in a closed system with a low presence or absence of oxygen and a specific pressure and temperature rate (Nartey and Zhao, 2014; Tan et al., 2015; Wang et al., 2020).

2.3.1 Preparation of biochar. Different processes can be utilized to convert biomass into biochar including, gasification, torrefaction, hydrothermal carbonization, and pyrolysis, where the selection of the appropriate process depends on the type and nature of the biomass and the required conditions of the process that suits the biochar production (Tan et al., 2015; Cha et al., 2016; Wang et al., 2020; Yaashikaa et al., 2020).

2.3.1.1 Gasification process. Gasification is the conversion of carbonaceous materials into 85% gaseous products known as synthesis gas (syngas)by decomposition using various gasification agents such as air, wet vapor, carbon dioxide, and oxygen at high temperatures (Vijayaraghavan, 2019). Also, this process produced liquid and solid products such as oil and char, respectively, where biochar production formed only 5% to 10% of biomass gasification products compared to other thermochemical processes (Cha et al., 2016). Gasification follows different steps, namely, (1) drying step to reduce the moisture content of biomass; (2) pyrolysis step to decompose the weak composition structure of biomass; (3) oxidation; and (4) gasification step (Cha et al., 2016; Yaashikaa et al., 2020).

2.3.1.2 Torrefaction process. The biomass torrefaction is conducted under a low heating rate (> 50ºC/min) and long residence time at a temperature ranging between 200 and 300 ºC in a free oxygen environment to remove CO_2 and O from the biomass and completely remove the moisture content (Cha et al., 2016; Yaashikaa et al., 2020; Wang et al., 2020). The process involves several steps that change gradually with temperature, namely, heating of biomass to reduce the moisture content at 100ºC, drying of heated biomass above 200ºC, torrefaction at 200ºC, and cooling (Yaashikaa et al., 2020).

2.3.1.3 Hydrothermal carbonization process. Hydrothermal carbonization is the mixture of biomass with water in a close reactor system at a temperature of 180ºC to 300ºC under high atmospheric pressure to produce hydrochar (biochar) (Tan et al., 2015). This process is considered to be cost-effective because it can convert biomass with moisture content such as animal manure and sewage sludge into biochar using low energy, excluding the drying step, compared to dry thermochemical processes such as gasification and pyrolysis, which require high energy to reduce or remove the moisture content (Tan et al., 2015; Chaet al., 2016; Yaashikaa et al., 2020).

2.3.1.4 Pyrolysis process. Pyrolysis is a decomposition process used to produce biochar, bio-oil, and synthesis gases in different percentages at a temperature between 400 °C and 1000°C in free oxygen conditions (Yaashikaa et al., 2020). Pyrolysis can be divided into two processes, namely fast pyrolysis, and slow pyrolysis, the heating rate in fast pyrolysis, analogous to its name is fast (above 300°C/min) at a short residence time (less than 60 min) at a temperature above 500 °C and generates a high yield of bio-oil and a low yield of synthetic gas and biochar (Vijayaraghavan, 2019; Wang et al., 2020). Slow pyrolysis, on the other hand, operates at a lower heating rate (5 to 7°C/min) with a longer residence time (above 60 min) and produces a higher yield of biochar (15–89%) than fast pyrolysis at temperatures ranging from 350 °C to 500 °C (Tan et al., 2016; Vijayaraghavan, 2019; Wang et al., 2020). Among all these production technologies, the pyrolysis process was found to be easy to preform and more effective for producing an acceptable yield of biochar (Wang et al., 2019).

The pyrolysis method produces biochar in three stages at varying temperatures, each of which has a significant impact on the physical and chemical properties and structure of the product (Ding et al., 2014; Cárdenas-Aguiar et al., 2017). The first stage (200 °C) involves the evaporation of moisture, which causes bond dissociation and the formation of different functional groups, such as the hydroperoxide group (H2O2), carboxylic group (-COOH), and carbonyl group (-CO). The second stage is the decomposition and devolatilization of feedstock polysaccharides (cellulose and hemicellulose) at a fast rate from 200 to 500°C. Moreover, the third stage is the degradation of strong chemical bonds of organic matter and lignin at temperatures above 500°C.

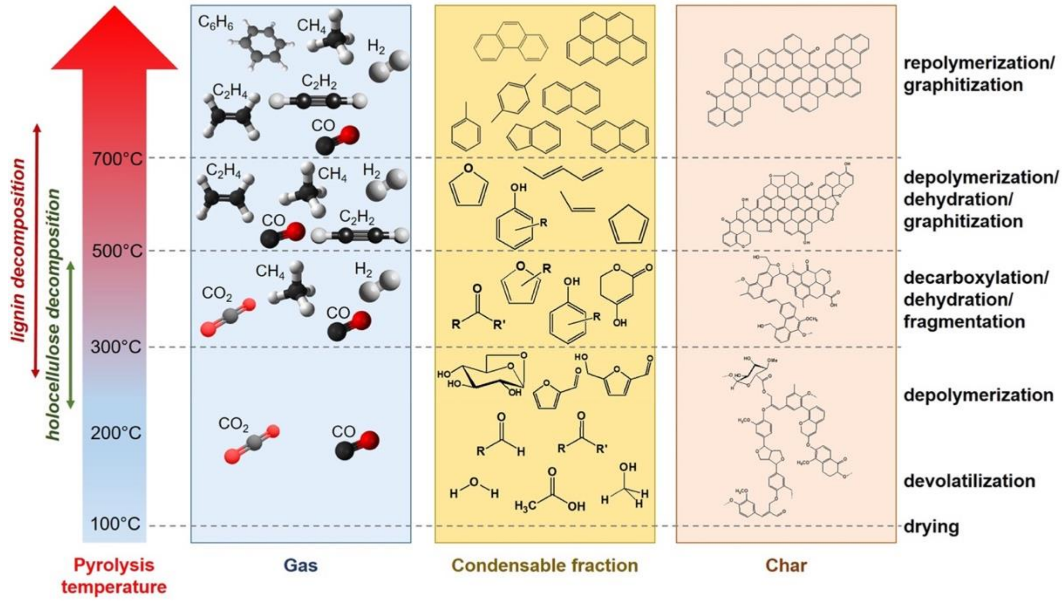

Figure 5. Evaluation of pyrolysis products with the increases of pyrolysis temperature (Giudicianni et al., 2021).

2.3.2 Factors affecting biochar production and properties. Several factors influence the production of biochar and its physicochemical characteristics, namely the source of feedstock, pretreatment of biomass, and three parameters of the thermochemical conversion processes, such as temperature, heating rate, and residence time (Nartey and Zhao, 2014; Vijayaraghavan, 2019).

The biomass feedstocks are the available materials composed of organic or inorganic materials found in the environment that can be converted into biochar due to their physicochemical properties (Yuan and Xu, 2011; Poo et al., 2018; Vijayaraghavan, 2019; Hoslett et al., 2019). Biochar feedstocks are obtained from different sources, namely plant sources, for instance, forest debris, plant wastes, marine plant species, animal sources such as animal manures, and municipal solid waste (Wang et al., 2019). Biochar is mainly produced from wastes from agricultural fields and helps in residues and disposal management systems (Tan et al., 2015). The physicochemical properties of biochar are heavily influenced by the feedstock resource and type, specifically functional groups, porosity, cation exchange capacity, pore size distribution, surface area, and elemental content (Sohi et al., 2010; Zhao et al., 2013). In addition, the moisture content is strongly affecting biochar production; feedstock with high moisture content can influence and inhibit the yield production of biochar and is found to be unsuitable because it requires a high amount of energy (Vijayaraghavan, 2019; Yaashikaa et al., 2020). However, biomass with low moisture content was found to be suitable to produce biochar because it requires a low amount of heat energy and production time, which is considered economically feasible (Yaashikaa et al., 2020). Also, the lignocellulose biomass composed of lignin, cellulose, and hemicellulose plays a role in biochar production, where high lignin and cellulose contents of feedstock are found to produce high yields of biochar with macropores and micropores respectively (Rangabhashiyam and Balasubramanian, 2019).

Pretreatment of biomass feedstock prior to biochar production is found to be essential where the reduction of particle size tends to increase yield production (Yaashikaa et al., 2020). Also, pretreatment affects the elemental concentration and composition of biomass; it enhances the carbon content and reduces the moisture content of biochar (Yaashikaa et al., 2020).

Biochar production is also influenced by the production technologies, mainly affected by operating and carbonization temperature, heating rate, and residence time of the process (Yaashikaa et al., 2020). The temperature may affect the structure and properties of biochar; as temperature increases, the fixed carbon content increases compared to oxygen, nitrogen, and hydrogen content, which are reduced because they are volatilized through the pyrolysis of biomass (Panwar et al., 2019; Yaashikhaa et al., 2020). Moreover, the high quality of biochar can be achieved under the high temperature of the process to remove volatile compounds, which in turn increases the carbon content, long residence time, and reduced heating rate (Wang et al., 2020). Furthermore, high pyrolysis temperatures led to an increase in biochar surface area, pH rate, volatile matter, and carbonization of feedstock. This, however, decreased the function group and cation exchange capacity (Tomczyk et al., 2020).

2.3.3 Physicochemical properties of biochar. The quality of biochar can be measured by its chemical and physical properties, namely carbon and nutrients content, porosity, functional group, surface area, surface morphology, cation exchange capacity, and pH rate; these properties exhibit differently among various feedstock namely plant source or animal source (Wang et al., 2020). The analysis of elemental content, structure and functional groups is essential to understand and measuring the impact of biochar on the environment and its interaction with metals (Yaashikaa et al., 2020). Several chemical and physical analyses of biochar can be obtained by using different analytical techniques to determine and test quantitatively and qualitatively the properties of biochar (Vijayaraghavan, 2019).

2.3.3.1 Physical properties and analysis of biochar. To further understand the biochar sorption mechanism; the physical characterization of biochar can be examined through different analytical methods namely, scanning electron microscopy (SEM), particle size distribution analysis, and Brunauer-Emmett-Teller (BET) analysis for surface area (Nartey and Zhao, 2014; Yaashikaa et al., 2020). The morphology of the biochar surface can be analyzed using SEM that gives information about the pore size distribution of biochar, and it is highly influenced by the production processes and temperature rate (Ma et al., 2016; Yaashikaa et al., 2020). In addition, the surface morphology of biochar is affected by the dehydration and volatilization processes that occur during the pyrolysis of biomass materials, Liang et al., (2016), investigated that the pyrolysis temperature has a strong effect on the pore structure and surface morphology, where the removal of volatile matter increased at temperature ranging between 200 and 500 ^{o}C during the formation of biochar which in turn enhance the production of pores opening. Moreover, the decomposition of chemical bonds can lead to the formation of more pores in the biochar structure.

The surface area of biochar is related to its porosity, and it can be obtained by BET analysis that indicates the capability of biochar to retain water, metals, and organic molecules (Yaashikaa et al., 2020; Guo et al., 2020). Biochar surface area, pore size distribution, and pore volume were found to increase with the temperature and residence time of the pyrolysis process because of the decomposition of organic matter that led to the formation of channel structure (Nartey and Zhao, 2014; Wang et al., 2019; Tomczyk et al., 2020). Ahmad et al., (2012) found a positive correlation between the temperature of the pyrolysis process, the surface area, and the porosity of biochar, where the elevation of temperature led to the increase of biochar surface area and void space. In addition, the source of biomass materials affects the surface area of biochar, for example, plant biomass contains organic carbon which in turn increase the porosity of biochar under heating condition (Wang et al., 2019).

2.3.3.2 Chemical properties and analysis of biochar. On the other hand, the chemical characterization of biochar can be analyzed by Fourier Transform Infrared Spectroscopy (FTIR) to determine the surface functional groups, elemental CHNOS analysis, and pH analysis (Wang et al., 2019; Guo et al, 2020; Yaashikaa et al., 2020). The surface functional groups of biochar comprise mainly carboxylic, hydroxylic, amide, and amine, which are highly influenced by the biomass source and temperature of the production process and can be examined by FTIR (Yaashikaa et al., 2020). According to Nartey and Zhao, (2014), the presence of some chemical functional groups can decrease with the increase of pyrolysis temperatures such as hydroxyl, carbonyl stretching, alkenes, and alkanes. Moreover, the reduction of functional groups occurs also due to the increase of carbonization degree under high pyrolysis temperatures (Wang et al., 2019). The cation exchange capacity of biochar which originated mainly from the functional groups implicates the ability of biochar to adsorb cationic contaminants, however, plant biochar that is produced at high temperatures causes a reduction in CEC and losses of the functional group due to the decomposition of lignocellulosic biomass and acidic functional groups also because of the formation of aromatic carbon (Wang et al., 2019; Guo et al., 2020; Tomczyk et al., 2020).

Biochar is composed mainly of different elements namely carbon which considers being the dominant element, hydrogen, nitrogen, and oxygen. The elemental concentrations depend mainly and strongly on the pyrolysis heating rate; according to Mohanty et al., (2013), the generation of biochar under a low heating rate was found to increase the percentage of carbon and hydrogen content more than the high heating rate. Furthermore, high temperature led to the reduction of oxygen, hydrogen, and nitrogen concentration, however, increases the concentration of carbon and other elements such as calcium, magnesium, potassium, and phosphorous (Wang et al., 2019). In addition, the elemental concentration of biochar depends also on the source of biomass, where animal ma nure has a low concentration of carbon compared to other elements, however, plant wastes contain high carbon content (Wang et al., 2019).

Biochar produced from different biomass materials demonstrated a pH value ranging from 5 to 12, the pH illustrates an expression of biochar composition of organic acids and water-soluble base cations, for instance, formic acid, acetic acid, sodium, potassium, and calcium ions (Guo et al., 2020). The pH of biochar is based on the mineral ash content (oxides or carbonates) and organic acids; where the high ash content and low organic acids due to pyrolysis methods shows a high pH value (> 7) (Wang et al., 2019; Guo et al., 2020). Furthermore, pH is affected by the pyrolysis temperature, a positive correlation was found between pH and temperature; according to Enders et al., (2012) the elevation of pyrolysis temperature led to the increase of pH higher than 7.5 due to the decomposition and vaporization of acidic functional groups and organic acids, respectively.

2.3.4 Biochar application in the environment. The addition of biochar to the environment, specifically in soil, causes an improvement in the physical and chemical properties, reduces the presence of contaminants, and enhances the quality of the soil (Burch, 2018; Naeem et al., 2019; Srivatsav et al., 2020; Yaashikaa et al., 2020; Ali et al., 2021). Biochar is characterized by high surface area and porosity, the presence of different functional groups, and pH (Tomcyk et al., 2020). Several studies have been conducted to investigate the applicability and efficiency of biochar as a remediator in contaminated soil (Igalavithana et al., 2019; Hashmi et al., 2019; Guo et al., 2020; Wang et al., 2021; Ali et al., 2021).

Biochar showed a great improvement in soil fertility and carbon dioxide sequestration; it enhances the structure of the soil and its productivity and properties, namely, pH, moisture content, aeration state, cation exchange capacity, and organic content (GuhaRay et al., 2019). Also, it reduces the emission of CO_2 and other greenhouse gases (GHG), which pose a significant threat to the environment by causing climate change and global warming (Tan et al., 2015; GuhaRay et al., 2019). In addition, biochar has a benefit on the economic level where it improves the sustainability of biomass production and enhances the bioenergy projects and agricultural industry by increasing the crop yield, which also improves the circular bioeconomy (Wang et al., 2020; Yaashikaa et al., 2020). Furthermore, the application of biochar considers a low-cost material, is simple and easy to use and requires low energy demand (Hayyat et al., 2016).

2.3.4.1 Remediation of heavy metal contaminated soil. Biochar has been demonstrated to be widely used for mitigating soil contaminated with heavy metal through the mechanism of stabilization and transferring them into less soluble and bio-accessible forms (Wang et al., 2019;

Guo et al., 2020). Additionally, Biochar is beneficially used to mitigate the impact of soil pollution since it has the ability to interact with different pollutants and restrict their mobility and bioavailability (Wang et al., 2020). Biochar plays a similar role as a chemical agent that reacts with heavy metals and converts them into precipitates, where the stabilization of heavy metals happens through different physical and chemical mechanisms, namely, adsorption, electrostatic interaction, ion exchange, precipitation, and surface complexation (Liu et al., 2018; Guo et al., 2020).

Physical adsorption occurs by the intermolecular force and is affected by the surface area of biochar and the pyrolysis condition that enhances the adsorption of heavy metals onto biochar (Wang et al., 2019). Biochar surface pores have a large diameter compared to heavy metal ions, which in turn increases their adsorption capacity to form either a monolayer or multilayer on the biochar surface. Shakya and Agarwal (2019) found that biochar prepared from pineapple peel using pyrolysis methods at different temperatures has the potential to adsorb chromium at a rate of 41.7 mg/g. In addition, Liu et al. (2019) used biochar produced from agricultural waste to remove lead (Pb). The results showed that biochar adsorbs 49.7 mg/g of Pb (II) because of several physical and chemical factors that contributed to removing Pb (II).

Biochar characterized with high negative charge can in turn improve the electrostatic interaction between soil and heavy metals; this mechanism depends on the soil pH, ionic radius, and point of zero charges (PZC) (Wang et al., 2019). The positive charge of heavy metals is electrostatically adsorbed onto the negative surface charge of biochar where it combines with functional groups containing oxygen (Ali et al., 2021). Qiu et al. (2008) investigated that the remediation of soil contaminated with lead by two different biochar produced from wheat and rice straw is highly effective due to the mechanism of electrostatic interaction between lead and negative charges on the biochar surface. Furthermore, ion exchange refers to the exchange of metal ions on the biochar surface with heavy metals. This chemical mechanism is affected by the biochar chemical properties, namely functional groups, and CEC, where the oxygen-containing group can ionize with hydrogen ions or nutrient elements such as sodium and calcium to exchange with heavy metal ions (Wang et al., 2019; Ali et al., 2021). Another mechanism that occurs during the addition of biochar into contaminated soil is precipitation, where the elemental composition of biochar reacts with heavy metals to form insoluble minerals that effectively lead to the immobilization of heavy metals (Shen et al., 2017; Wang et al. 2019).

Heavy metal precipitation is related to the physical and chemical changes that occur in contaminated soil after the addition of biochar, where hydrolysis of heavy metals is enhanced at higher pH values and the concentration of water-soluble metals is reduced (Wang et al., 2019; Guo et al., 2020). The elevation of soil pH happened due to the presence of carbonate in biochar, which increases the alkalinity of contaminated soil.

Biochar plays an effective role in ameliorating the physicochemical properties of soil, where the addition of biochar in the soil led to the increment of soil pH and surface area which in turn decreases the dissolution and leaching of heavy metal, however, increases the physical adsorption capacity (Wang et al., 2019; Ali et al., 2021). The application of biochar in contaminated soil can have a positive effect on soil properties through the enhancement of water holding capacity, CEC, particle and bulk density, and surface area, minimum and maximum effect of biochar on soil properties can be demonstrated in Table 3 which was adapted according to several studies (Yu et al.,2013; Blanco-Canqui, 2017; Tomczyk et al., 2020; Nkoh et al., 2021). In addition, the presence of biochar can change the functional groups in soil, add more micronutrients that improve crop yields and reduce the leaching of essential nutrients due to the increase of CEC in soil (Tomczyk et al., 2020). According to Zhan et al. (2019), the application of biochar in contaminated farmland soil led to a significant increase in nutrient elements and a reduction of lead and cadmium in soil and plants. Another example of the application of biochar is tabulated in Table 4, which illustrates the results of biochar remediation produced from different feedstocks on contaminated soil.

Table 3. Effect of biochar on the chemical and physical properties of soil.

Soil parameter	**Minimum**	**Maximum**
Soil pH	3.99	8.40
CEC (mmol/Kg)	51.5	177.2
Water holding capacity	16.8%	274.1%
Bulk density (Mg/m^3)	1.06	1.68

CEC: cation exchange capacity.

Table 4. Different Biochar feedstock and remediation effect on contaminated soil.

Feedstock	Temperature	contaminants	Remediation effect	References
Orange bagasse	500 °C	Cu	Removal of 28% of copper from fallow field soil	Gonzaga et al., 2020
Sugarcane bagasse	400-450 °C	Cd	Reduced the bioavailability of cadmium and enhance the yield of soybean	Mohamed et al., 2019
Rice straw	500 °C	Cr	Removal of 22.3% of chromium in paddy soil	Zhou et al., 2019
Maize straw	500 °C	Cd	Reduced the concentration of cadmium by 50.4% in paddy soil	Zhang et al., 2019
Wheat straw	300 °C	Hg	Removal of 26% Hg in farmland soil	Xing et al., 2019
Oat hull	300 °C	Cu	Removal of 68% of copper from sedimentary alfisol.	Moore et al., 2018
Sugarcane bagasse	500 °C	Cd Cr	Removal of 40% Cd and 49% Cr from contaminated agricultural soil.	Bashir et al., 2018
Rice straw	500 °C	As	Reduced the concentration of arsenic by 49-68% in paddy field soil.	Yin et al., 2017

Feedstock	**Temperature**	**contaminants**	**Remediation effect**	**References**
Wheat straw	500 ^{o}C	Cd	Reduce the concentration of cadmium by 57 to 86%	Chen et al., 2016
Pine bark	420 ^{o}C	Cu	Removal of 81% copper from Cu-contaminated topsoil of wood preservation site.	Oustriere et al., 2016
Wood of *Eucalyptus saligna*	450 ^{o}C	Ni	Reduce the concentration of nickel (Ni) in soil and improve the growth of plants	Rehman et al. 2016
Orchard pruning	500 ^{o}C	As	Removal of 68% of arsenic in contaminated mine soil	Beesley et al., 2013
Rice straw	300 ^{o}C	Pb	Increase adsorption capacity of lead onto biochar surface and reduces the activity of Pb in soil	Jiang et al., 2012
Oakwood	400 ^{o}C	Pb	Reduce 75% of Pb bioavailability	Ahmad et al., 2012
Cotton stacks	450 ^{o}C	Cd	Decrease in cadmium bioavailability through adsorption and precipitation	Zhou et al., 2008

Biochar can also change the biological properties of soil through the improvement of microbial activities and fungi growth, as reported by Anyanwu et al, (2018) biochar application in soil affects positively the plant and root growth, and soil biota. In addition, the interaction between biochar and microbes has altered the element cycle in soil and increased the availability of bacteria, which in turn enhances the decomposition of biological materials in soil (Ali et al., 2021). Furthermore, Huang et al. (2019) investigated that biochar prepared from wheat straw has enhanced the availability of nutrient elements, which in turn improves the photosynthetic rate and formation of grains of wheat (*Triticum aestivum*). In another study, Hashmi et al. (2019), found that the addition of waste leaf biochar to soil has strongly improved the crop growth of *Pisum sativum* and the uptake of nutrients and water. Moreover, the invasive plant species known as *P. juliflora* has the potential to purify contaminated soil. Kaur and Sharma (2019) converted *P. juliflora* into biochar to treat soil polluted with polyaromatic hydrocarbon PHA. A pot experiment was carried out over six months to determine the potential of biochar in the remediation method. The results illustrated that biochar significantly enhanced the soil quality and plant growth and also reduced the abundance of PHA with high removal efficiency.

2.4 The mesquite, *P. juliflora:*

2.4.1 Origin and distribution. *Prosopis* is a plant genus that is extended from the family of Fabaceae (Leguminosae) and exists in 44 different species, including *P. juliflora, P. pallida, P. glandulosa,* and *P. chilensis* (Trenchard et al., 2008; Ravhuhali et al., 2021). *Prosopis* is a native flowering plant that originated in different parts of America, namely, Mexico, the Caribbean, Colombia, Costa Rica, and Venezuela. However, it has been introduced in different arid and semi-arid countries; for instance, in South and North Africa, Australia, East Asia countries, and Middle East countries such as Kuwait, Bahrain, Iraq, and Qatar (Chapman et al., 2019). The rapid and wide distribution of *Prosopis* species mainly occurs through animals' feces, where some animals such as camels and goats feed on the plant pods and release the undigested seeds with their feces, which in turn remain in the soil to germinate later (Shiferaw et al., 2014). In addition, humans sought to introduce the *Prosopis* all over the world for various reasons, including the need for timber and wood for furniture and fuel, respectively, for medical purposes, providing fodder for animals, and a source of food for humans (Ravhuhali et al., 2021). Furthermore, it reduces the effect of desertification, enhances the habitat, and establishes green landscapes, which increases the vegetation globally (El-Keblawy and AlRawai, 2007).

P. juliflora is a plant species known commonly as mesquite and found to be invasive in most regions around the globe that grow in a wide range of climatic conditions, namely arid and semi-arid regions (Chapman et al., 2019). It is also a fast-growing xerophyte plant that grows and tolerates harsh environmental conditions such as drought and high-saline soil (Kazmi, 2009; Shanwad et al., 2015). Since the mesquite represents an invasive species, it leads to a number of negative impacts that affect other native plant species, animals, and the environment (Shanwad et al., 2015; Chapman et al., 2019). In the State of Qatar, *P.juliflora* is considered one of the highly invasive plant species introduced in the 1950s for several purposes; for instance, as a hedge plant, to increase the vegetation on the roadsides, and as an ornamental (Usman, Abu-Dieyeh, and Al-Ghouti, 2019; Chapman et al., 2019). For example, the spread of *P. juliflora* possesses a threat to the germination of native plants in Qatar. For example, it affects the growth and germination rate of *P. cineraria* through the allelopathic effect resulting from the growth of *P. juliflora* (Bibi and Abu-Dieyeh, 2016; Elazazi et al., 2016).

P. juliflora is characterized by different ecological traits that enable it to grow and survive under harsh environmental conditions, namely, drought, saline, and alkaline soil, different soil structures and textures such as stony soil, and live in a wide range of rainfall regions (Shanwad et al., 2015; Patnaik et al., 2017). There are several factors that allow *P. juliflora* to tolerate different environmental conditions and become invasive. These factors include the rapid growth and germination rate of the seeds; high absorption rate of water by the roots; leaves that can be recovered quickly after drought seasons; and the production of allelochemicals that possess a threat to the production and germination of other plants (Walter, 2011; Bibi and Abu-Dieyeh, 2016; Patnaik et al., 2017). In addition, *P. juliflora* can survive in drought regions and salty soil because it has a defense mechanism including the control of the opening of stomata, gas exchange, and osmotic adjustment (Ravhuhali et al., 2021).

2.4.2 Morphology of *P. juliflora*. *P. juliflora* is represented as an evergreen and perennial tree with a height reaching between 3 m and 12 m. It is characterized by long cylindrical branches, an ample number of green bipinnate leaves with 6 to 29 leaves per pinna, produces flattened and curved yellow pods, twisted green to brown stems, and the roots grow and spread both vertically and horizontally (Sawal, Ratan, and Yadav, 2004; Patnaik et al., 2017; Hassen et al., 2017; Chapman et al., 2019). Moreover, the bark tends to be rough with a dull red color, and the inflorescence of *P. juliflora* produced is green in color and changes to yellow when ripe. It is axillary and cylindrical in shape, and it is found with sizes ranging from 8 cm to 10 cm (Sawal et al., 2004; Gallaher and Merlin, 2010).

P. juliflora produces a yellowish fruit in legume pods form with 1–16 pods per inflorescence, where the external and internal structure are composed of three different components, including epicarp, mesocarp, and endocarp, where the seeds exist (de Brito Damasceno et al., 2017). The proportion of each layer varies greatly from one pod to another, where the thickness and color of the exocarp change, the chemical composition of the fleshy mesocarp varies, and the fibrous endocarp contains a different number of brown seeds (Dave and Bhandari, 2013). Furthermore, the pods are green when immature and change to yellow to brown when mature, with a slightly curved or coiled shape, additionally, the length is measured to be 10 cm to 40 cm long and contains around 25 seeds (Gallaher and Merlin, 2010; Patnaik et al., 2017). The seeds are small in size, with an ovoid shape that consists of three layers, namely, seed coat (episperm), endosperm, and cotyledon. They exist in a brown color with a hard and thick coat that enables the seeds to tolerate harsh environmental conditions for a long time (Dave and Bhandari, 2013).

2.4.3 Chemical properties. *P.juliflora* produced a high concentration of nutrients, flavonoids, and different percentages of lignocellulose composition, where the wood is made up of 40-45%, 11-28%, and 25-30% of cellulose, lignin, and hemicellulose, respectively (Dave and Bhandari, 2013). In addition, the leaves produced are unpalatable and composed of various chemical substances, namely, 2% tannins, 20% crude proteins, and 2.2% alkaloids such as *juliflorine* and *juliflorcicine* (Ali et al., 2012; Patnaik et al., 2017; de Brito Damasceno et al., 2017).

The pods produced by *P. juliflora* are composed of highly nutritious values for wide varieties of animals, consisting of 3–6% of digestible protein and 66–69% of digestible dry matter content (Sawal et al., 2004). Moreover, it contains various concentrations of carbohydrates, crude protein and fiber, amino acids, fat, vitamin C, and ash. It also possesses different mineral concentrations required for animal feed, namely, calcium, phosphorus, and high iron, zinc, and copper (Sawal et al., 2004; Ali et al., 2012; Shitanda et al., 2013; Al-Harthi et al., 2018). A study done by da Silve et al. (2010) showed that the pods are composed of 56%, 9%, and 2.1% of sugar, protein, and lipids, respectively, with high palatability.

P. juliflora seeds are characterized by a high concentration of tannin (6.81 % - 9.15%), a total protein that contains different amino acids and fatty acids such as trace amount of methionine, phenylalanine (2.0 g/100 g seed - 2.8 g/100 g seed), linoleic (35 % - 36 %) and oleic acids (37% to 39%) (Kathirvel and Kumudha, 2011). Seeds are also made up of several essential elements, for example, calcium, magnesium, potassium, and phosphorous. Furthermore, gum with valuable sugar components is produced known as seed galactomannan, which is considered a natural polysaccharide found in the endosperm part (Dave and Bhandari, 2013; Rincon et al., 2014). According to Shitanda et al. (2013), a high concentration of galactose, fucose, xylose, and glucose is found in the seeds' gum. Seed gum can be used in the pharmaceutical industry, paper, and textile manufacturing, and oil field industries (Vieira et al., 2007; Rincon et al., 2014). In addition, bioethanol can be produced from the seeds through the fermentation of sugar content by yeast (*Saccharomyces cerevisiae*) (Sindhu and Gnanavel, 2016).

2.4.4 Benefit of *P. juliflora* on the environment. The growth and spread of *P. juliflora* globally tends to have a positive impact on the environment where it enhance soil fertility and productivity because of the organic matter provided, increases the moisture content of the soil, promotes the enzymatic activity of microorganisms, prevents the erosion of the soil, and stabilizes the sand dune (Dave and Bhandari, 2013; Walter and Armstrong, 2014; Patnaik et al., 2017). Furthermore, *P. juliflora* reduces the soil salinity and wind speed with 14% and 22% moisture losses by evaporation, which also plays a role in carbon dioxide sequestration (Patnaik et al., 2017). The concentration of organic carbon and nitrogen in soil under *P. juliflora* canopies was found to be 13% and 45%, respectively, thereby improving soil fertility (Patnaik et al., 2017). *P. juliflora* acts as a phytoremediator plant by bioaccumulating heavy metals such as iron, zinc, copper, cadmium, and chromium in the soil (Khan et al., 2015; Michel-Lopez et al., 2016; Usman et al., 2016; Patnaik et al., 2016). The invasion of *P. juliflora* in soil has been reported to improve soil quality due to its ability to fix nitrogen and increase nutrient content (Edrisi, El-Keblawy, and Abhilash, 2020).

Furthermore, *P. juliflora* is considered as a source for different purposes, namely, a source of fuel through the utilization of wood, where wood was used to feed the power plants as a source of energy and fuel in India. Additionally, it produces biofuels such as bio-oil and biodiesel (Walter and Armstrong, 2014; Patnaik et al., 2017). Another useful purpose of *P. juliflora* determined as a source of food and feed; where the flour produced from the pods, which is widely used due to its high nutritional value and suitability for baking, also obtained to be a cheap alternative and economically feasible as a feed source (da Silva et al., 2010; Ali et al., 2012; de Gusmao et al., 2016). Moreover, the animals fed more in the pods because they contained a high concentration of carbohydrates and protein (Ravhuhali et al., 2021). Furthermore, *P. juliflora* has the potential to be used as a biopesticide against plant diseases and has been shown to be effective as an antibacterial against various pathogens such as E. coli (TajBakhsh et al., 2015; Patnaik et al., 2017). According to a study done by Saleh and Abu-Dieyeh (2021), *P. juliflora* antimicrobial activities have been observed by the extracts of leaves and fruit that inhibit the growth of various microorganisms, namely, bacteria, yeast, and fungus. Therefore, *P. juliflora* extract potentially protected the growth of cherry tomatoes and proved its efficiency to be substituted for anti-spoilage chemicals. In addition, *P. juliflora* could be used as a biosorbant to remediate contaminated soil and remove pollutants like dyes and heavy metals (Patnaik et al., 2017).

2.4.5 Impact of *P. juliflora* on the environment. The rapid and easy dispersion, poor management of *P. juliflora* and the negative impact it possesses on the native environment and socio-economically have made this plant species invasive (Hussain et al., 2020). *P. juliflora* has the ability to colonize large land areas due to several factors, including high seed dispersal by livestock, rapid growth in rainfall and drought regions with temperature variations, unsuitable cultivation lands, and the production of allelochemicals that negatively affect other plant species (Sawal et al., 2004; Patnaik et al., 2017; Abdulahi et al., 2017; de Brito Damasceno) Furthermore, the invasion effect increases the mortality of native plant species because of the competition for the resources namely water and nutrients (Ravhuhali et al., 2021). The growth of *P. juliflora* has been reported to extensively reduce the groundwater level because of the complex root system (Edrisi et al., 2020). A study was done in the Afar region in Ethiopia that quantified the consumption of water by *P. juliflora*, and the results determined that the water volume consumed was approximately 3.3 billion m3/year; this high consumption posed a threat to the water security in the rural livelihoods (Shiferaw et al., 2021) Another study was done by Howari et al., (2022), to study the invasion effect of *P. juliflora* on the availability of fresh groundwater in different regions in the United Arab Emirates, where the results demonstrated a dramatic increase in groundwater consumption by 7372% from 1990 to 2019, which therefore caused a depletion of freshwater availability in the country. Moreover, the severity of the *P. juliflora* invasion has impacted different ecosystem services, for instance, the provisioning services, where it negatively affects food security and agropastoralism (Edrisi et al., 2020). For instance, the consumption of immature pods by animals led to different symptoms such as fever, dehydration, and weight loss, and might even lead to death (Sawal et al., 2004).

2.4.6 Management of *P. juliflora* impact. Different countries have made efforts to eradicate the growth of *P. juliflora* through various mechanisms, namely mechanical, biological, and chemical methods. However, these methods have been found to be expensive and ineffective (Abdulahi et al., 2017; Pandey et al., 2019; de Brito Damasceno et al., 2020). A mechanical method includes the removal of plants' roots, burning, and cutting. A study was done in Brazil by Goncalves et al. (2015) to manage the growth of 320 trees of *P. juliflora* through effective methods, namely cutting, grinding, and burning. Another study revealed that the grinding of pods ensures the full utilization and digestion of seeds by animals without passing feces and prevents their widespread (Sawal et al., 2004).

The chemical method is the utilization of chemical agents through the application of herbicides to control the growth of *P. juliflora*, according to Shanwad et al. (2015), different types of herbicides were used from 2009 to 2011 to manage and reduce the growth of *P. juliflora*, and the results illustrated an effective control of the growth rate. On the other hand, biological methods include the application of insects and pathogens to damage the seeds of *P. juliflora* and prevent their germination. For instance, in Australia, various insect species were used to deteriorate the reproduction of the tree and negatively affect the mature pods and seeds (Abdulahi et al., 2017; Chapman et al., 2019). On the other hand, the utilization of *P. juliflora* for different purposes, such as commercial utilization, is considered the best option to manage and control the growth and invasion of *P. juliflora* through the frequent harvesting of all components of the plant in order to reduce its dominance (Patnaik et al., 2017; Ravhuhali et al., 2021). For instance, Saleh and Abu-Dieyeh, (2022), investigated that water-soluble leaf ethanolic extract of *P. juliflora* reduces the spoilage of strawberries, extends their shelf-life, and enhances the quality of the storage.

In addition, *P. juliflora* has been used as an adsorbent for the remediation of contaminated soil or wastewater, either as raw material or in chemical or physical treated forms (Patnaik et al., 2017). A study done by Kottapalli and Majeti (2009) to determine the capability of *P. juliflora* seed powder in the remediation of lead-contaminated water showed effective removal of lead where the adsorption capacity was obtained to be 40.3 mg/g at pH 6 of aqueous solutions. In contrast, Jayaram and Prasad (2009) found that the seed powder removed 81.79% of lead from an aqueous solution. Furthermore, *P. juliflora* powder removed 18.2 mg/g of copper and 11.5 mg/g of zinc at pH 5 and pH 6, respectively, from an aqueous solution (Habtegebrel and Khan, 2018). Moreover, Nair and Vinu (2016) used biochar produced from *P. juliflora* wood to remove two different dyes, namely, Remazol Brilliant Blue R and methylene blue, where the adsorption capacities were found to be 83 mg/g and 91 mg/g, respectively. Additionally, Halnor et al. (2013) investigated that *P. juliflora* leaf, which was treated with nitric acid was capable of removing 89% of copper from an aqueous solution. However, Gopal et al. (2014) treated an aqueous solution polluted with dye (Direct Red 23) using activated carbon prepared from *P. juliflora*. The results obtained showed that the adsorbent was highly capable of remediating the solution with an adsorption capacity equal to 90.9 mg/g at 30 ^{o}C and 109.9 mg/g at 45 ^{o}C.

Chapter 3: Methodology

3.1 Materials collection of *P. juliflora* pods.

P. juliflora pods (fruits) were collected from Qatar University Campus (25°22'30.0"N 51°29'23.3"E) and washed with tap water followed by distilled water to ensure the removal of any impurities. The pods were dried overnight inside the oven at 50 ^{o}C and then pulverized by a grinder to transfer them into a fine powder for biochar preparation.

3.2 Preparation and characterization of biochar.

3.2.1 Slow pyrolysis and biochar yield. Prepared *P. juliflora* pods were weighed and then pyrolyzed in a muffle furnace (Nabertherm Compact Tube Furnace, Germany) at different temperatures and times as illustrated in Table 5 with a continuous supply of nitrogen gas. The samples were left inside the furnace to cool down before collecting the biochar. The biochar was sieved through 1 mm and 0.5 mm mesh sizes then stored in an airtight container and labeled as PJP (*P. juliflora* pods) biochar.

Table 5. Preparation of biochar from *P. juliflora* pods using a tube furnace.

Time (Min)	Temperature	Process
00	20 ^{o}C	Start Nitrogen Flow at R.T
20	20 ^{o}C	Start increasing temperature at a rate of 10^{o}C/min till reaches 300 ^{o}C
50	300 ^{o}C	Start increasing temperature at a rate of 5 ^{o}C/min till reach 500 ^{o}C
90	500 ^{o}C	Keep the temperature stable at 500^{o}C for 30 min
120	500 ^{o}C	Start Cooling
420	20 ^{o}C	

The percentage yield of biochar was calculated using the following equation (Stella Mary et al., 2016).

$$\text{Yield (\%)} = \frac{m_{biochar}}{m_{raw}} \times 100$$

Where ($m_{biochar}$) is the mass of biochar (g) and (m_{raw}) is the mass of raw biomass (g).

3.2.2 Physical and chemical characterization of biochar. The biochar was characterized for elemental analysis using carbon, hydrogen, and nitrogen analyzer (Thermo Fisher, Flash 2000 Elemental Analyzer CHNS/O). Furthermore, the functional groups on the surface of biochar were revealed by Fourier-transform infrared spectroscopy (FTIR) before and after the batch experiment. FTIR Perkin Elmer- UATR analytical instrument was used and the recorded spectra of biochar were in the wavenumber ranges from 400 $cm\text{-}^{1}$ to 4000 $cm\text{-}^{1}$.

The morphology and surface area were examined using Scanning Electron Microscopy (Nova NanoSEM 450, FEI) and Brunauer–Emmett–Teller (BET) respectively (Niinipuu, 2019; Yaashikaa, 2020). In addition, cation analysis of biochar was done following the extraction process by adding 0.5 g of dry ground biochar in a 50 mL tube filled with distilled water, then the tube was shaken manually and sonicated for 20 min in a sonication bath. The tube was shaken in a shaker for 20 min and centrifuged to separate the liquid from the biochar, followed by a filtration process. The filtered sample was diluted and submitted for ionic analysis using Ion Chromatography (Metrohm 850 Professional IC) at Qatar University Central Laboratories Unit (QU-CLU).

3.3 Preparation of nickel and lead stock solution

The stock solution of nickel (1000 ppm) was prepared by adding 2.21 g of nickel chloride ($NiCl_2$) that dissolved in 1000 mL of distilled water in 1 L borsoil volumetric flask.

The stock solution of lead (1000 ppm) was prepared by adding 1.59 g of lead nitrate ($Pb(NO_3)_2$) into 1000 mL distilled water in 1 L borsoil volumetric flask.

3.4 Batch equilibrium study (pilot study)

3.4.1 Effect of initial concentration on the adsorption capacity of lead and nickel onto biochar. A batch experiment was conducted to investigate the optimum initial concentration and conditions for the adsorption of Pb and Ni onto the biochar surface (Shafiq, Alazba, and Amin, 2021). The experiment was performed under different initial concentrations of heavy metals. In 100 ml borosilicate glass bottles, different initial concentrations of Ni and Pb solutions were prepared (50, 100, 200, 400, 600, 800, and 1000 mg/L) with a final volume of 50 mL and each initial concentration was carried out with three replicates. A 0.05 g of biochar was added, and the glass bottles were placed in the mechanical shaker at controlled conditions with 145 rpm for 24 hours at a room temperature of 25^{o}C. After 24 hours the samples were filtered for further analysis using centrifuging. The filtered solution was diluted and analyzed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Optima 7300 DV (PerkinElmer, USA) at the Central Laboratories Unit (QU-CLU), Research and Graduate Studies Sector, Qatar University.

The removal percentage of heavy metal was examined through the following equation (Francy et al.,2020):

$$\text{Heavy metals removal \%} = \frac{(Ci-Ce)}{Ci} X\ 100 \qquad \text{equation 1}$$

Where Ci and Ce mean the initial concentration and equilibrium concentration respectively both in mg/Kg.

In addition, the adsorption capacity at equilibrium was obtained by the following equation (Wang, Xia, and Lu, 2017):

$$\text{qe} = \frac{(Ci-Ce)m_o}{m_t} \qquad \text{equation 2}$$

Where Ci (mg/g) is the initial concentration of the adsorbate; Ce (mg/L) is the equilibrium concertation of the adsorbate; m_o (g) is the mass of the soil, and m_t (g) is the biochar mass.

3.5 Collection and preparation of artificially contaminated soil sample

3.5.1 Soaking method. A collected regular soil sample characterized as sandy soil with 90% was collected from Qatar University campus (25°22'29.6"N 51°29'24.1"E), sieved by passing through a 2 mm mesh to generate particle size ranged between 0.5 mm to 0.125 mm, the sieved soil then placed in a polythene bag, autoclaved, and sterilized two times at 130 ^{o}C for one hour each under 15 lbs pressure (AUT12, Vertical autoclave, USA). The pH was measured to be 7.19 (alkaline soil). Moreover, a preliminary metal analysis was conducted for the regular soil, which demonstrated that the soil contains 7.49 mg/kg of Pb and 19.03 mg/kg of Ni which reflected to be less than the international threshold standard limit of Pb and Ni in soil (see section 1.1).

For the study of the effect of initial concentration using an incubation experiment, regular sterilized soil samples (50 g) were placed in 100 mL borosilicate glass bottles, then different initial concentrations (50, 100, 200, 400, 600, 800, and 1000 ppm) of Pb and Ni solutions (50 mL) prepared from a stock solution of ($Pb(NO_3)_2$) and ($NiCl_2$) were added to the glass bottles. The soil samples were submerged with Pb and Ni solutions to allow the contaminants to permeate into the soil and ensure mixing with the soil (Karkush, and Ali, 2020; Kamal, Mahmood, and Duja, 2021). The soaked soil samples were incubated in dark conditions at 25 ^{o}C for seven days to ensure heavy metals stabilization. After the incubation process, the soil samples were oven-dried at 40 ^{o}C, and then 0.25 g of soil was digested through a strong acid microwave digestion system MARS 6 (CEM Corporation, USA) and followed by ICP-OES Optima 7300 DV (PerkinElmer, USA) analysis for the determination of the artificially contaminated soil samples with lead and nickel. The strong oxidizing acids used in the digestion process are HNO_3, HCl, and HF. The acids were added as follows: 6.0 mL of concentrated HNO_3, 2.0 mL of concentrated HCl, and 2.0 mL of concentrated HF. The samples were digested and analyzed at (QU-CLU).

3.6 Incubation experiment

3.6.1 Effect of initial concentration on remediation mechanism. The artificially contaminated soils (50 g) with different initial concentrations, namely 50, 100, 200, 400, 600, 800, and 1000 mg/Kg were placed in 100 mL borosilicate glass bottles, mixed with 0.05 g of biochar, and 15 mL of distilled water was added to maintain soil moisture (Alaboudi, Ahmed, and Brodie, 2019). The glass bottles were sealed with parafilm and, to ensure soil aeration; small holes were made. The samples were carried out in a closed chamber at 25 ^{o}C for 30 days. Every 10 days, 0.5 g of soil samples were randomly collected from each bottle and oven-dried at 40 ^{o}C. The concentrations of lead and nickel in the soil samples were determined using ICP-OES Optima 7300 DV (PerkinElmer, USA), by dissolving the soil samples to form a liquid solution that can be analyzed by the analytical method using Microwave Digestion System MARS 6 (CEM Corporation, USA) at (QU-CLU). This experiment was performed in triplicate (A total of 22 samples for Ni, and 22 samples for Pb were analyzed).

3.7 Pot experiment

To assess and evaluate the efficiency of *P. juliflora* biochar on the remediation of Pb and Ni from the soil as well as the effect on plant growth, a pot experiment using tomato plant (*Solanum lycopersicum*) was conducted. The experiment was carried out under six different treatment levels using regular and artificially contaminated soil (see description in section 3.5.1) shown in Figure 6, namely, Treatment 1A (negative control: regular soil without biochar), Treatment 2A (positive control: lead-contaminated soil without biochar), Treatment 2B (positive control: nickel-contaminated soil without biochar), Treatment 3A (lead-contaminated soil with 0.05 g of biochar), Treatment 3B (nickel-contaminated soil with 0.05 g of biochar), and Treatment 4A (regular soil with 0.05 g of biochar). Each treatment level was conducted with six replicates.

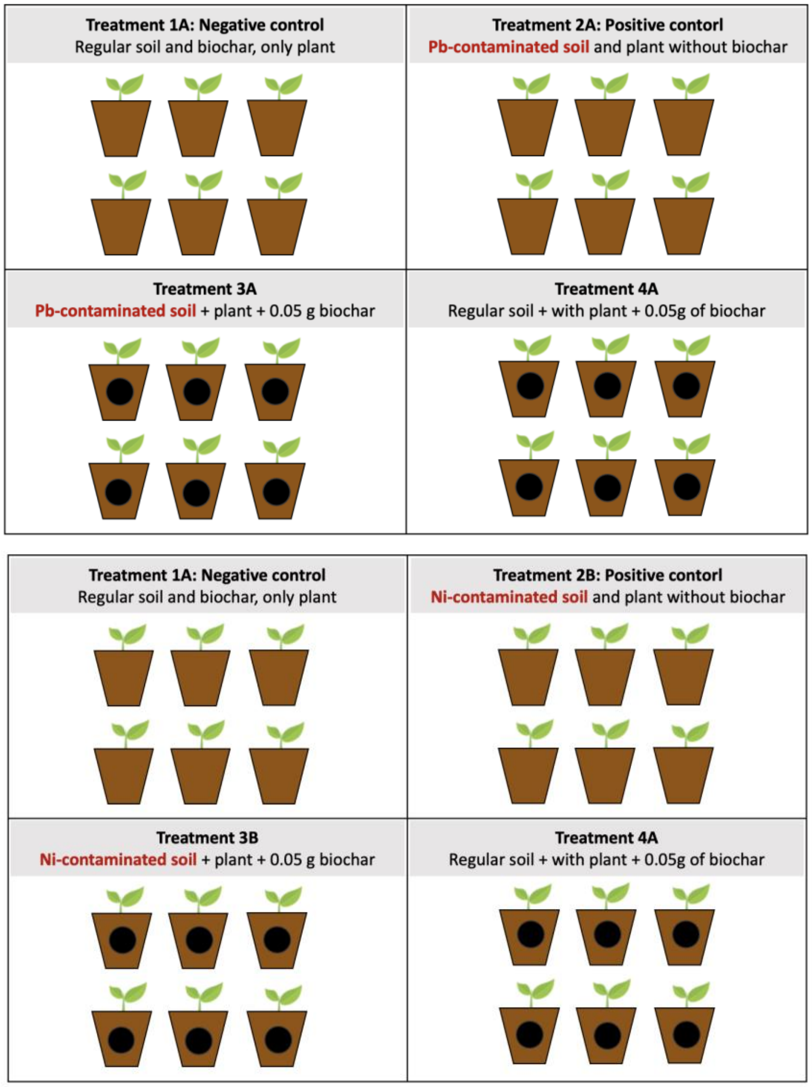

Figure 6. Illustrative diagram of the pot experiment under six different treatment levels.

Biochar and contaminated soil were homogenized in plastic containers prior to the pot experiment. Each pot was filled with a total mass of mixed soils (40% potting soil and 60% Ni-loaded and Pb-loaded soil) (see section 3.5), 0.05 g of biochar, and a number of tomato seedlings were sown in each pot. The pots were placed in a greenhouse under a controlled environment of 25-30 ^{o}C and 30-50% relative humidity. Moreover, the pots were irrigated with tap water four times per week to maintain the moisture content at water holding capacity.

Different growth parameters were measured during the course of the experiment and on weekly basis namely, the height of the plant, the number of leaves per plant, and the chlorophyll content of leaves using a chlorophyll meter (Konica Minolta, Spad-502Plus). For chlorophyll content (µmol/m^2), three leaves were chosen from the medium zone along the plant height of each seedling and the average of the three readings was calculated and reported.

3.8 Soil and plant physicochemical characterization

3.8.1 Soil physicochemical analysis. The $pH_{solution}$ of the soil was determined by adding 20 g of air-dried soil in 50 mL distilled water and the solution was stirred in a mechanical shaker under controlled conditions namely 145 rpm for one hour at room temperature 25 ^oC. The value for soil pH before the adsorption process was 7.19. The pH of contaminated soil with Ni and Pb after the incubation experiment was 7.78 and 8.00, respectively, which indicated the increase in pH after the addition of biochar.

The surface properties of soil were examined using different analytical methods namely, Fourier transform infrared (FTIR) spectroscopy analysis was used to identify the functional groups on the surface of the soil before and after the soaking process using FTIR Perkin Elmer- UATR (400 – 4000 cm^{-1}) at (QU-CLU). Furthermore, the morphology texture of the soil was examined using Scanning Electron Microscopy (Nova NanoSEM 450, FEI) at (QU-CLU).

3.8.2 plant physicochemical analysis. After the pot experiment, the above and below-ground parts (shoots and roots) of the tomato plants were collected, thoroughly washed with distilled water and then dried in an oven at 70 ^oC for five days. The dried samples were weighed and tabulated. After weighing, the dried materials were ground to form fine particles for further analysis.

In addition, the soil samples were oven-dried at 50 ^{o}C and sieved to less than 2 mm. The dried soil and plant samples (0.25 g) were chemically analyzed for Pb and Ni determination, by using microwave digestion (System MARS 6 CEM Corporation, USA) method then the digested materials were analyzed by ICP-OES Optima 7300 DV (PerkinElmer, USA) at (QU-CLU) (Beesley et al., 2013).

3.9 Statistical analysis

One-way ANOVA was carried out using SPSS software at 0.05 level for the effect of Pb and Ni on the growth of tomato plant with and without biochar treatment. The interaction between the variables, as well as any significant differences between the sample means, were investigated using the ANOVA test. At $P \leq 0.05$, the means were separated using Tukey's test. All the experiments were conducted in six replicates and the results were expressed in average value.

Chapter 4. Results

4.1 Chemical and physical characterization of artificial contaminated soil

4.1.1 Infrared (IR) spectroscopy analysis. Fourier transform infrared (FTIR) is considered a quantitative analytical method used to study the bonding mechanisms of different molecules, namely, minerals, organic and inorganic components, and metal oxides on soil surfaces. Figure 7 illustrates the functional groups of the regular soil from Qatar University (control soil) and artificially contaminated soil with lead and Ni (Pb-loaded soil and Ni-loaded soil). Functional groups were examined using FTIR with spectra ranges between 4000 cm^{-1} and 400 cm^{-1} that cover several classes of bonds. The broad bands in Figure 8 from 3700 cm^{-1} to 3100 cm^{-1} show the hydrogen bond (O-H) region. On the other hand, the broad peak observed in Figure 7 at 1398 cm^{-1} indicates the presence of organic matter and oxygen. Moreover, the low-intensity peak at 976 cm^{-1} can be ascribed to the OH group and vibration of silicates ($SiO_4{}^2$). Furthermore, the small peak shown in Figure 7 at 885 cm^{-1} is associated with carbonate ($CO_3{}^{2-}$) and nitrates (NO^{3-}). Additionally, the peak at 687 cm^{-1} corresponds to the presence of symmetrical bending vibration of Si-O.

As shown in Figures 7 and 8, after soaking the soil with Pb and Ni solutions, all of the peaks in the control soil sample were shifted and increased in intensity, which can be attributed to metal binding with the soil chemical components. Peaks located in the wavenumber between 3700 cm^{-1} and 3100 cm^{-1} have been shifted, and the intensities have increased for both Pb-loaded soil and Ni-loaded soil, as can be observed clearly in Figure 8. The observed change of 1398 cm^{-1} peak intensity in Figure 7 increases after the addition of heavy metal solution to the soil, which can be attributed to the strong interaction between heavy metals and the functional groups in the soil. In addition, a shifted peak was observed at 972 cm^{-1} for Pb-loaded soil and 977 cm^{-1} for Ni-loaded soil after the soaking process. Moreover, an increase in peak intensity at 885 cm^{-1} has been obtained and slight shifts occurred towards 869 cm^{-1}and 871 cm^{-1} for lead and nickel, respectively. This indicated metal sorption in the soil. The small shifts and slight increase in peak intensity at 687 cm^{-1} to 709 cm^{-1} and 713 cm^{-1} demonstrate the binding of soil surface compounds with Pb and Ni, respectively.

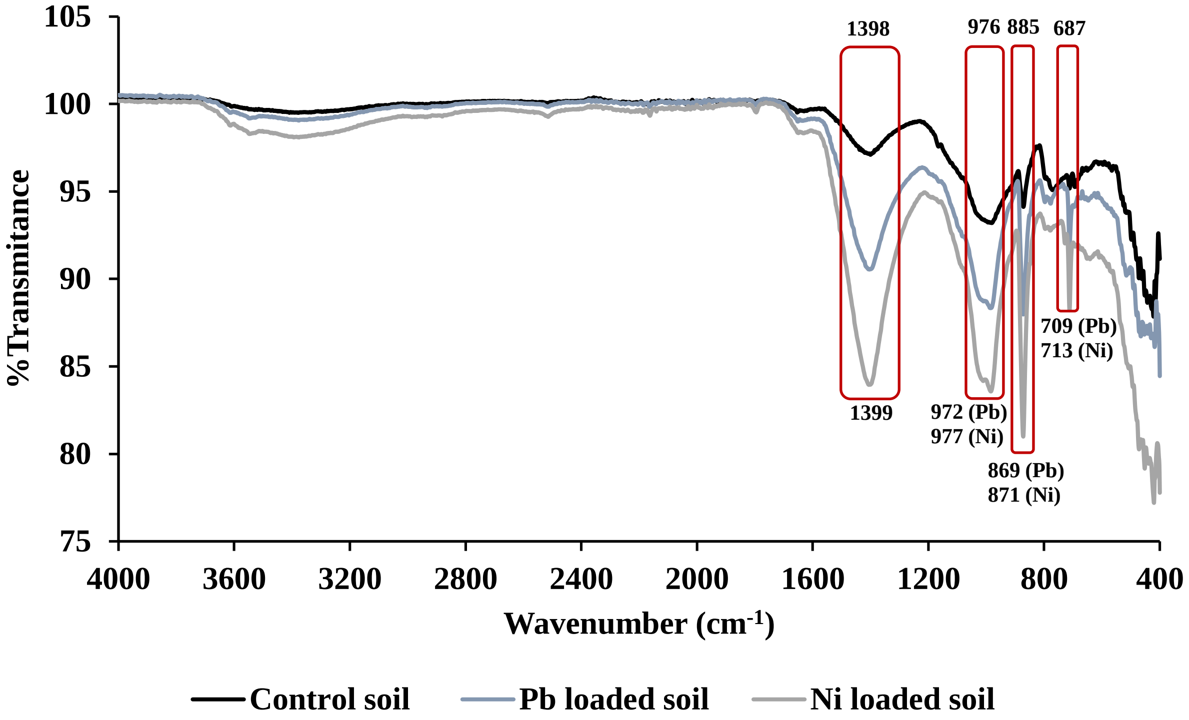

Figure 7. FTIR spectra (4000 cm^{-1} to 400 cm^{-1}) of the soil before heavy metals soaking method (soil control) and after soaking with Pb (II) and Ni (II) solution.

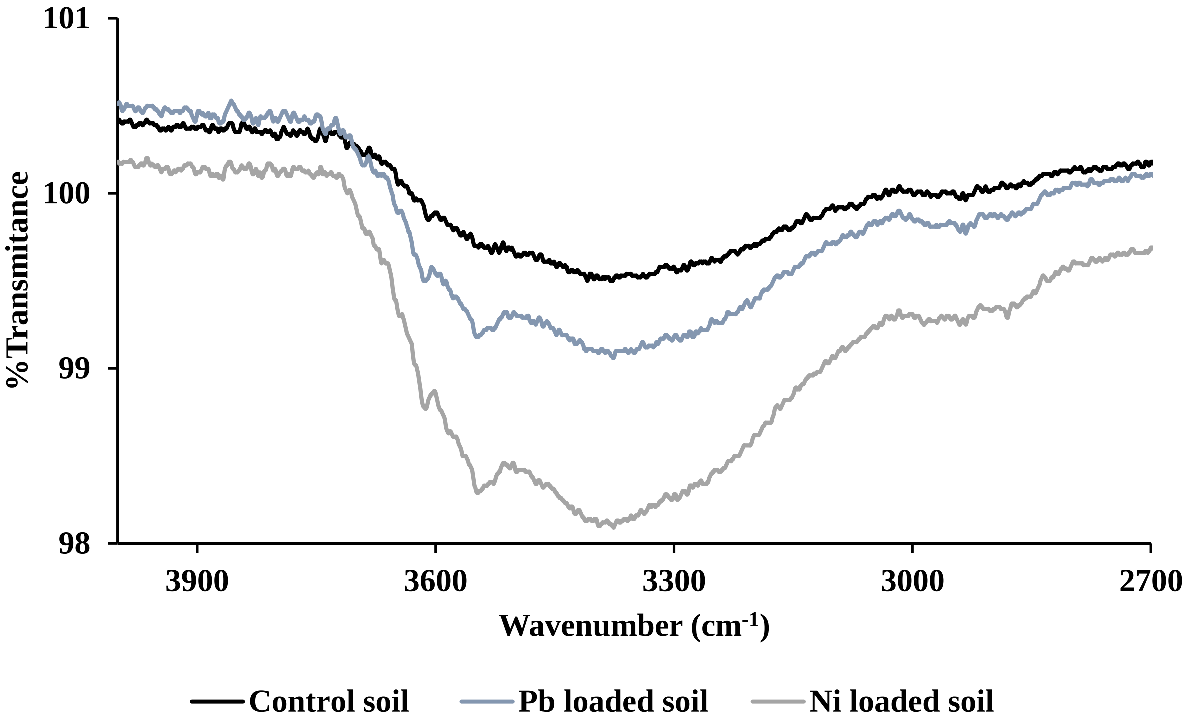

Figure 8. FTIR spectra (4000 cm^{-1} to 2700 cm^{-1}) of the soil before heavy metals soaking method (soil control) and after soaking with Pb (II) and Ni (II) solution.

4.1.2 Surface morphology analysis. Soil morphology before and after the soaking method with Pb and Ni was examined and scanned through various magnification modes namely, 2500x, 5000x and 10,000x illustrated in Figure 9 using Scanning Electron Microscopy. Figure 9 (ABC) demonstrates the regular soil morphology that appeared with a branch-like shape clearly observed in Figure 9 (A and B), in addition, the soil is characterized by its rough microstructure, non-uniformed shape, and void space.

After soaking soil with lead and nickel for seven days, it can be observed from Figure 9 (DEF) and (GHI) the high precipitation of Pb (II) and Ni (II) on soil surfaces, and this can be attributed to the porous structure of soil particles. Furthermore, morphological changes on the soil surface indicated that the structure had been distorted, and FTIR analysis in Figure 7 confirmed the adsorption of Pb (II) and Ni (II) into the soil surface (see section 4.1.1).

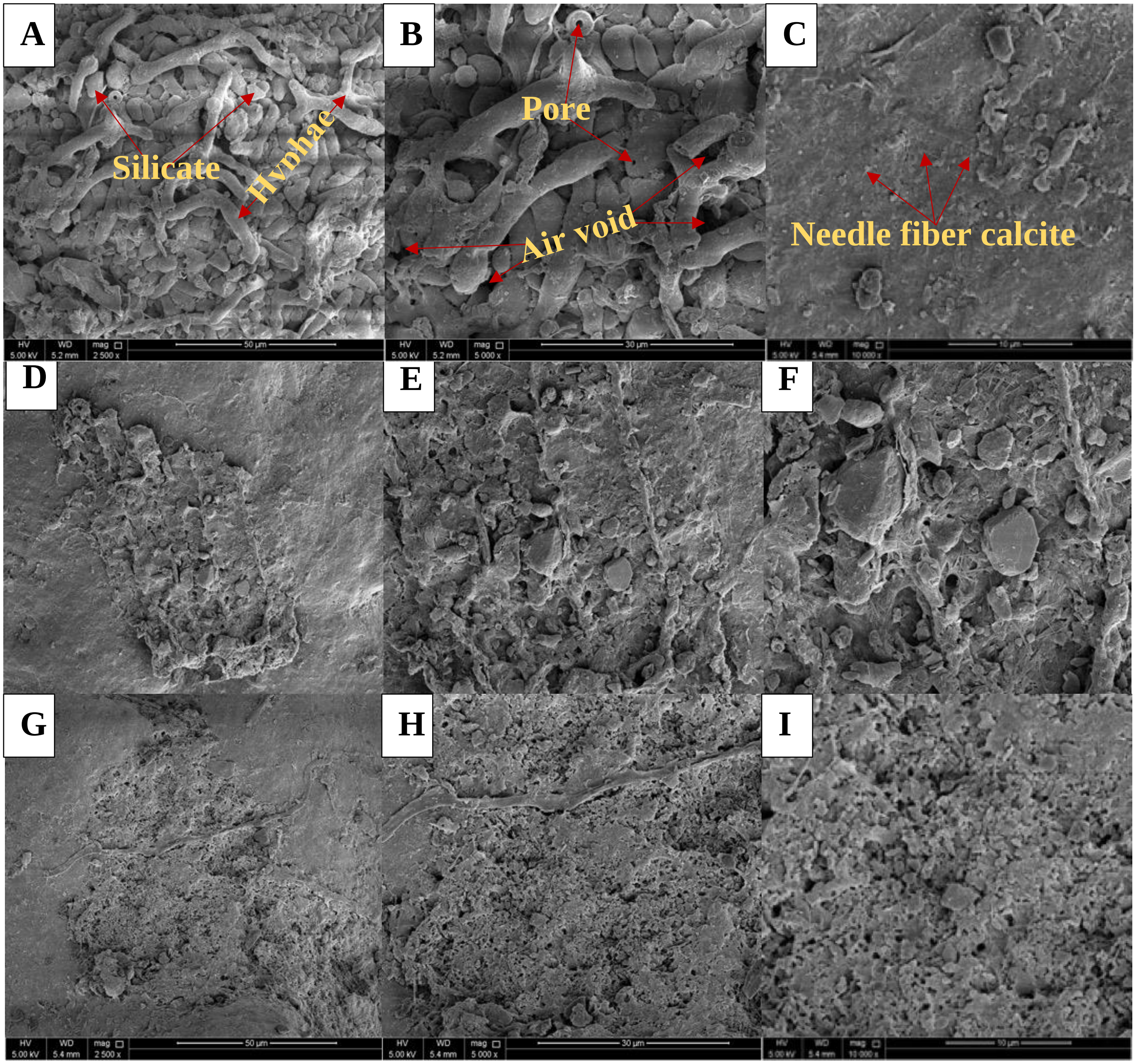

Figure 9. Scanning Electronic Microscopy (SEM) of control soil (ABC) before the soaking method, (DEF) Pb-loaded soil, and (GHI) Ni- loaded soil at 2500x, 5000x, and 10,000x magnifications.

The bulk density and particle density of soil were measured by weighing and calculating the mass and volume of the soil sample as tabulated in Tables 6 and 7.

Table 6. The bulk density of soil samples.

Mass of graduated cylinder	**Mass of graduated cylinder and soil**	**Mass of soil**	**Volume of uncompacted soil**	**Volume of compacted soil**	**Bulk density of soil**
43.0 g	71.3 g	28.3 g	18 mL	15 mL	4.7 g/cm^3

Table 7. The particle density of soil samples.

Volume of water	**Mass of soil**	**Volume of water with soil**	**Volume of soil particles**	**Particle density of soil**
25 cm^3	28.3 g	48 cm^3	23	1.2 g/cm^3

4.2 Batch experiment (pilot study)

4.2.1 Effect of initial concentrations. The effect of initial concentration on the adsorption of lead and nickel ions by biochar was determined with varying solution concentrations of 50, 100, 200, 400, 600, 800, and 1000 mg/L and with 0.05 g of adsorbent. The results in Figures 10 and 11 illustrate that the highest removal percentage was 99.4% for lead and 70.5% for nickel, respectively, corresponding to the initial concentration of 50 mg/L for both metals. Figure 10 demonstrated that the removal percentage of Pb (II) was slightly decreased with the increase in initial concentration from 99.4% to 95.9%. On the other hand, the percentage removal of Ni (II) in Figure 11 decreased dramatically from 70.5% to 4.9% with the increases in initial concentration, and this attributed to the reduction of the available and binding sites on the surface of the biochar.

Furthermore, according to Figures 10 and 11, it is demonstrating the adsorption capacity (qe) of Pb (II) and Ni (II) adsorbed onto biochar, where the adsorption capacity increases with the increase of the Pb concentration in Figure 10 from 50 to 1000 mg/L, and the highest qe (mg/g) was 959.9 mg/g in 1000 mg/L. This occurred because of the availability of the active sites on the surface of the adsorbents. In contrast, the maximum Ni (II) adsorption capacity shown in Figure 11 was achieved in the initial concentration of 800 mg/L; decreased with the increase of initial concentration because of the less availability of sites on the adsorbent surface at higher initial concentration namely 1000 mg/L, which in turn lower the binding mechanisms.

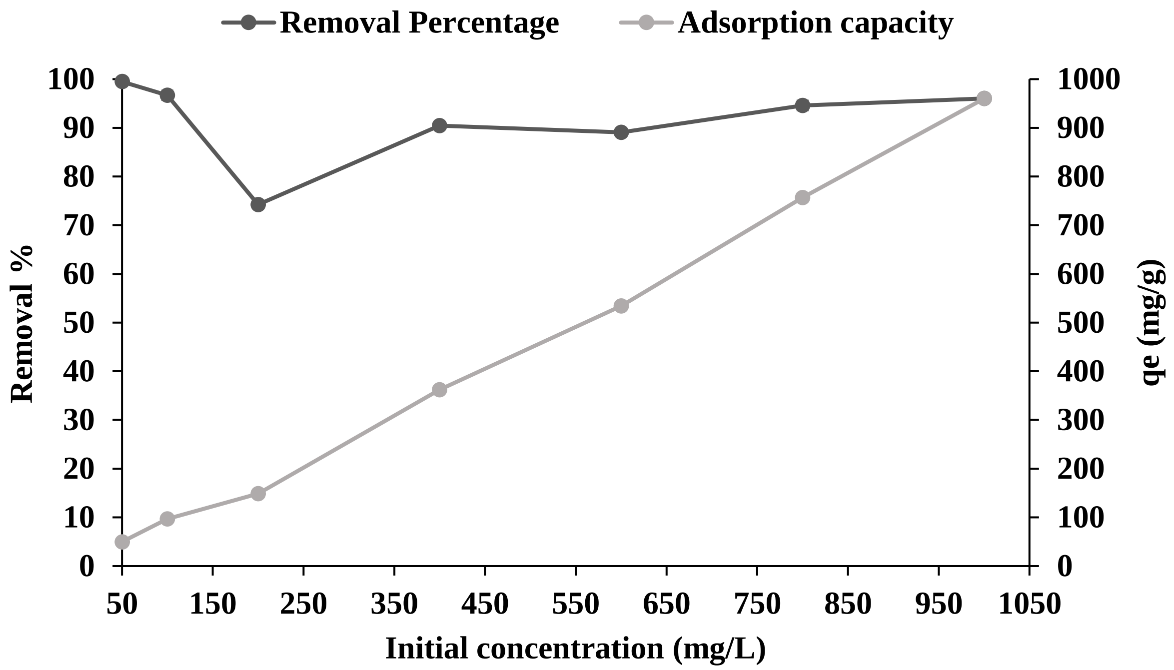

Figure 10. Effect of initial lead concentration (mg/L) on the removal efficiency and metal adsorption capacity (mg/g) of biochar for lead. Mean values are averages from three replicates (n = 3) ± SEM.

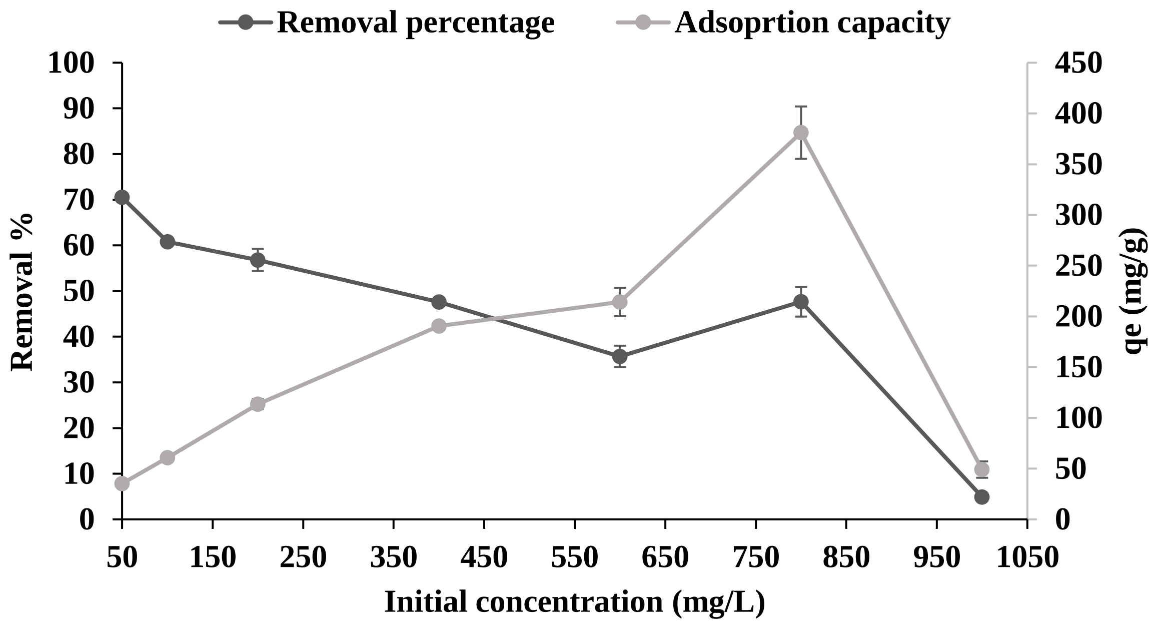

Figure 11. Effect of initial nickel concentration (mg/L) on the removal efficiency and metal adsorption capacity (mg/g) of biochar for nickel. Mean values are averages from three replicates (n = 3) ± SEM.

4.2.2 Effect of equilibrium concentrations. Figure 12 demonstrates the adsorption equilibrium of Pb (II) and Ni (II), where the maximum adsorption capacity of Pb (II) in Figure 12A was obtained to be 959.9 mg/g at an equilibrium concentration of 40 mg/l. On the other hand, as can be seen from Figure 12B, the highest adsorption capacity of Ni (II) was 381.06 mg/g at 418.93 mg/L. This can be attributed to the restricted active site available at a higher equilibrium concentration.

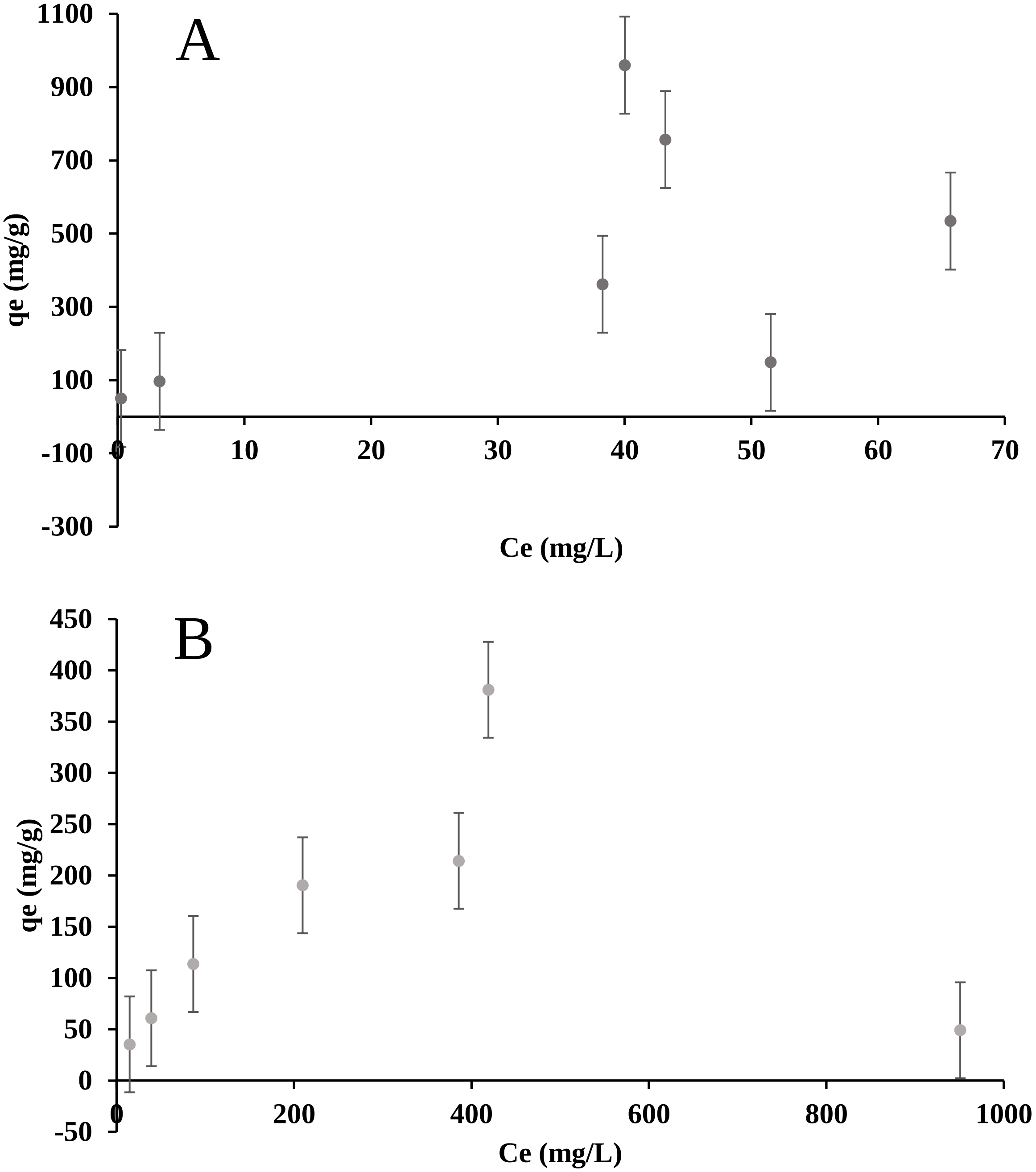

Figure 12. Adsorption capacity (mg/g) of (A) lead and (B) nickel on biochar at equilibrium concentration (mg/L) in aqueous solution.

4.3 Biochar surface characterization and heavy metal adsorption

4.3.1 Effect of biochar surface functional groups on heavy metals adsorption. The functional groups of biochar before the adsorption process were analyzed by FTIR and the corresponding spectra (4000 cm^{-1} - 400 cm^{-1}) are shown in Figure 13. The small peaks from 1617 cm^{-1} -1621 cm^{-1} are assigned to C=O and C=C stretching. The peak at 1400 cm^{-1} corresponded to C-H. The small peak at 881 cm^{-1} and 694 cm^{-1} reflected the presence of the C-H functional group. After the application of biochar into artificial contaminated aqueous solutions of Pb and Ni, FTIR analysis of biochar resulted in some changes in the various peak intensity and shapes that were attributed to the interaction between the two contaminants Pb (II) and Ni (II) and the surface functional groups of biochar. The peak at 1617 cm^{-1} was shifted to 1552 cm^{-1} and 1556 cm^{-1} for Pb (II) and Ni (II) respectively after adsorption, which indicates the availability of C=O and C=C groups. Moreover, a strong intensity change was observed at band 1400 cm^{-1} after the adsorption of Ni (II) with 1389 cm^{-1} compared to Pb (II) where the peak disappeared. In addition, the intensity of peak 881 cm^{-1} assigned to the presence of the C-H group increased after the adsorption of Pb (II) and Ni (II). Additionally, changes were determined at peak 694 cm^{-1} which slightly shifted to 744 cm^{-1} with high intensity and to 683 cm^{-1} after the adsorption of Pb (II) and Ni (II) respectively. These results proved that Pb (II) and Ni (II) interacted with the functional groups on the surface of biochar during the adsorption process.

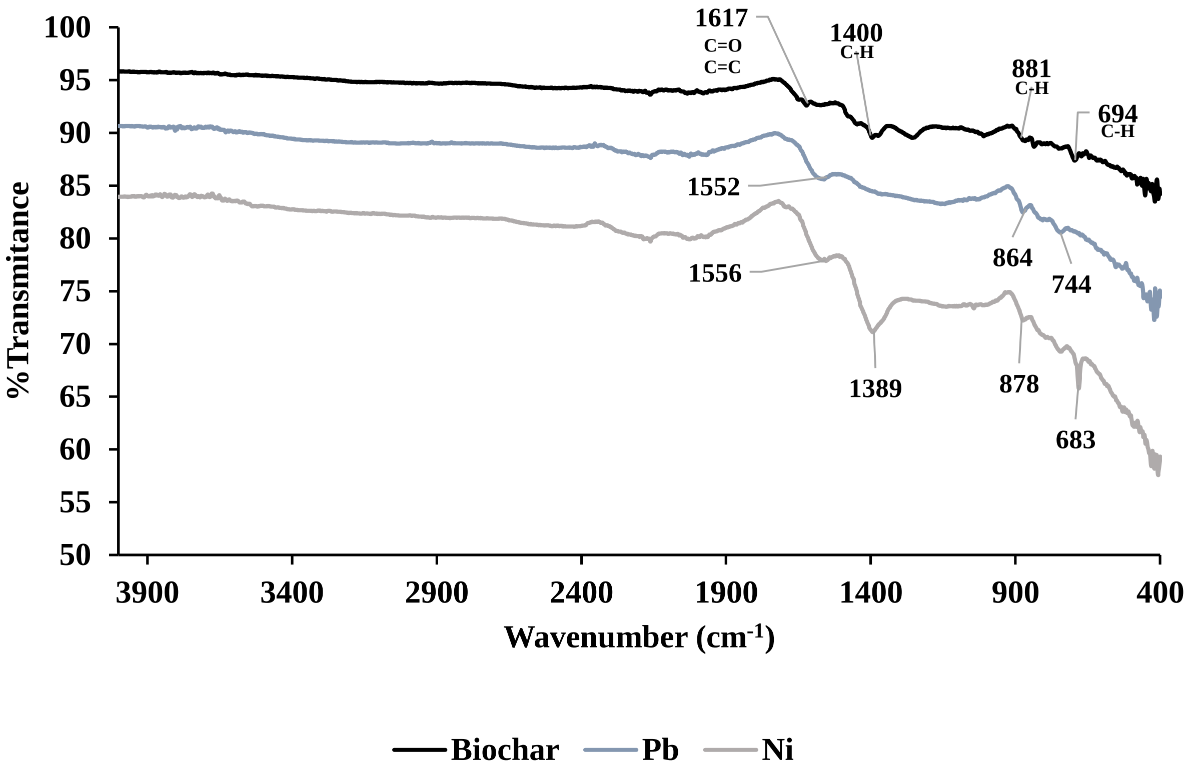

Figure 13. FTIR spectra of biochar derived from *P. juliflora* pods before and after the adsorption of Pb (II) and Ni (II) from synthetic contaminated aqueous solution.

Table 8. Absorption frequencies of functional groups in *P. juliflora* biochar

Wavenumber (cm^{-1})	**Functional groups**
1617	Carboxyl group (C=O) Aromatic group (C=C)
1400	C-H
881	Aromatic C-H
694	C-H

4.3.2 Effect of biochar morphology on heavy metals adsorption. The surface morphology of biochar at different magnification scales (2500 x, 5000 x, and 10000 x) before and after the adsorption on Ni (II) and Pb (II) was observed using SEM analysis shown in Figure 14. Biochar surface texture is characterized by a heterogeneous rough and hollow rod-like structure that illustrates the presence of various channels where it enhances the formation of different pore sizes. Therefore, improving the adsorption of heavy metals because it is providing a large surface area. SEM images after the adsorption of Pb (II) in Figure 14 (DEF) demonstrate white precipitation on the biochar surface. On the other hand, Figure 14 (GHI) illustrated the Ni-loaded onto the biochar surface, and the SEM results revealed the deposition and precipitation of the adsorbate on the biochar surface.

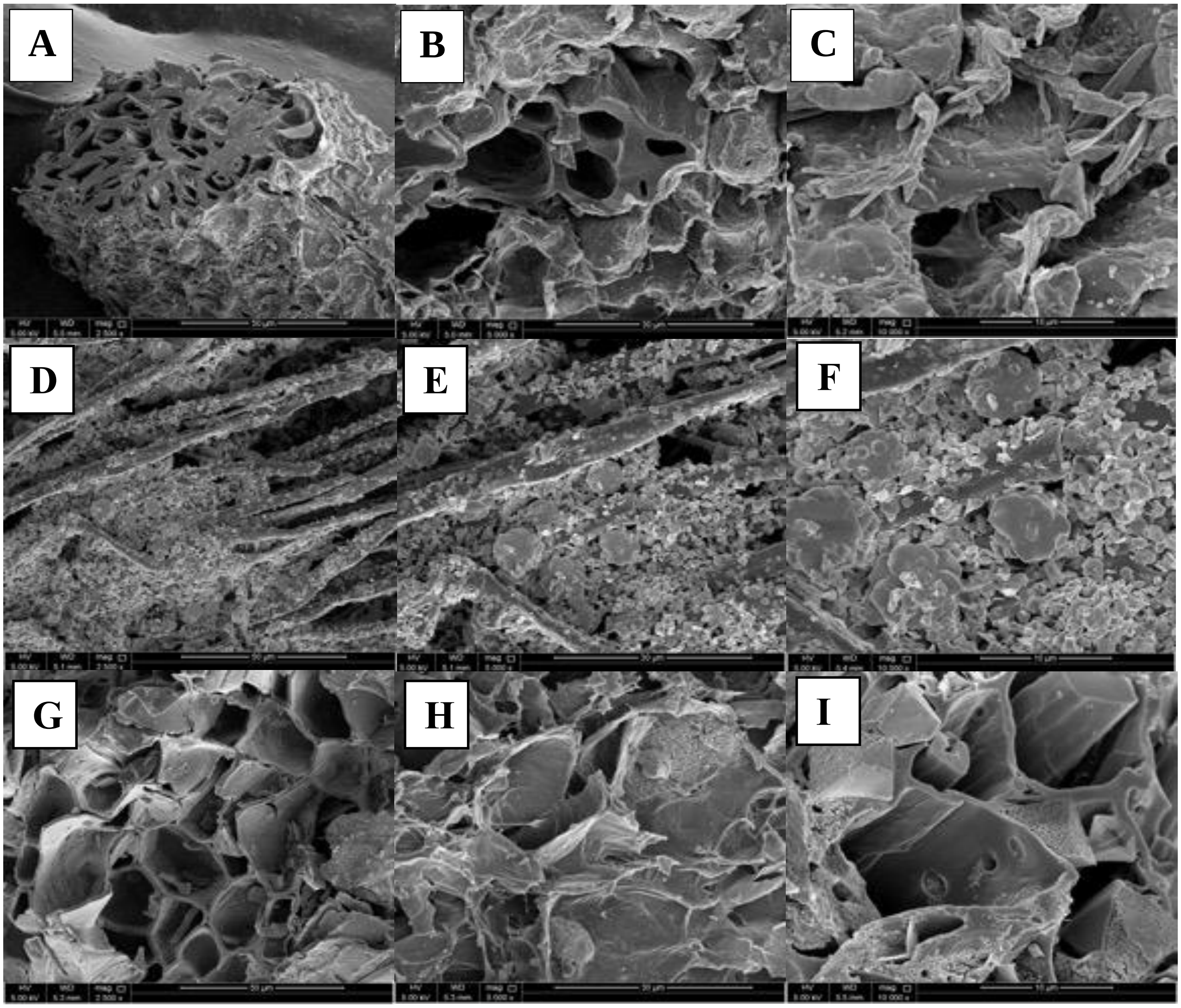

Figure 14. Scanning Electronic Microscopy (SEM) of *P. juliflora* biochar (ABC) before the adsorption process, (DEF) after adsorption of lead, and (GHI) after adsorption of nickel at 2500x, 5000x, and 10,000x magnifications.

4.4 Incubation experiment

4.4.1 Effect of initial concentrations. Figure 15 depicts the capacity of Pb adsorption onto the biochar surface for 30 days at various initial concentrations. The qe (mg/g) increased from 9.49 mg/g to 270 mg/g as the initial Pb (II) concentration in the soil increased from 24.39 mg/g to 685.6 mg/g, indicating strong adsorption of Pb (II) with the available sites on the biochar surface. On the other hand, the adsorption capacity of Ni (II) using biochar is illustrated in Figure 16, where the qe (mg/g) increased from 19.12 to 149.95 mg/g with the increases of initial Ni concentration in the soil from 47.79 mg/g to 375.8 mg/g; illustrating the strong ability of biochar and the available sites on the biochar surface to adsorb Ni (II). The greatest adsorption capacity for Pb (II) and Ni (II) were observed in higher initial concentrations at 685.6 mg/g and 375.8 mg/g respectively.

Furthermore, Figure 15 and Figure 16 demonstrate the percentage of stabilization efficiency of Pb (II) and Ni (II) in the soil after the application of biochar for 30 days at different initial concentrations. The stabilization efficiency of Pb (II) was found to fluctuate from 97.25% to 99.07% and for Ni (II), the stabilization efficiency ranged from 99.5% to 100% under different initial concentrations. This can be attributed to the increase in soil pH from 7.19 to 8.01 after being incubated with biochar.

4.4.2 Effect of equilibrium concentration. Figure 17 illustrates the adsorption equilibrium of (A) Pb (II) and (B) Ni (II). It can be demonstrated that the highest adsorption capacity of Pb (II) and Ni (II) was 270.62 mg/g and 149.95 mg/g at an equilibrium concentration of 6.13 mg/g and 0.91 mg/g, respectively. These results indicated that biochar sites become saturated at a high equilibrium concentration of Pb (II) compared to Ni (II).

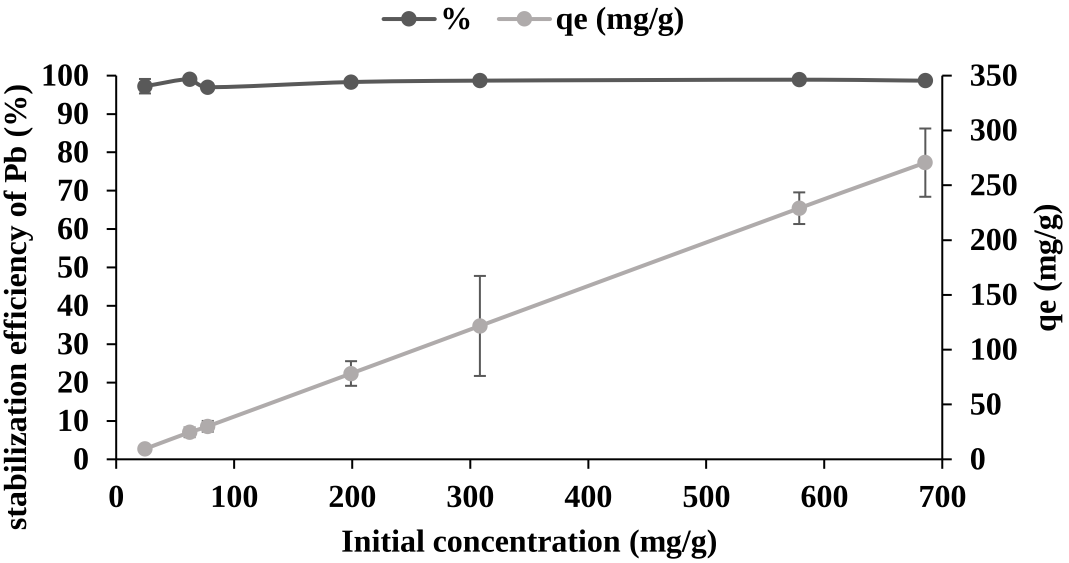

Figure 15. The stabilization efficiency of Pb and adsorption capacity (mg/g) by biochar under different initial concentrations in soil (mg/g). Mean values are averages from three replicates (n = 3) ± SEM.

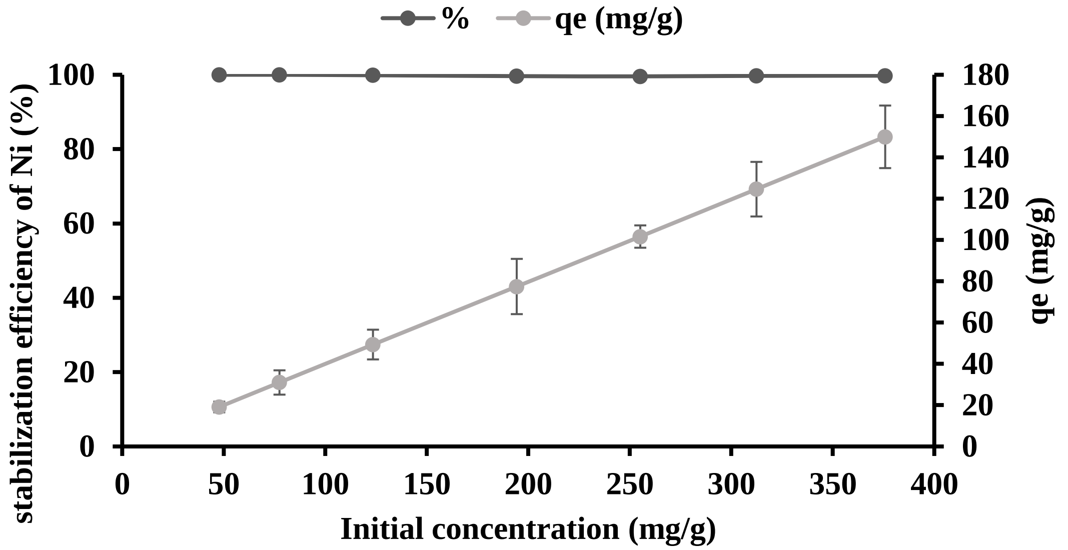

Figure 16. The stabilization efficiency of Ni and adsorption capacity (mg/g) by biochar under different initial concentrations in soil (mg/g). Mean values are averages from three replicates (n = 3) ± SEM.

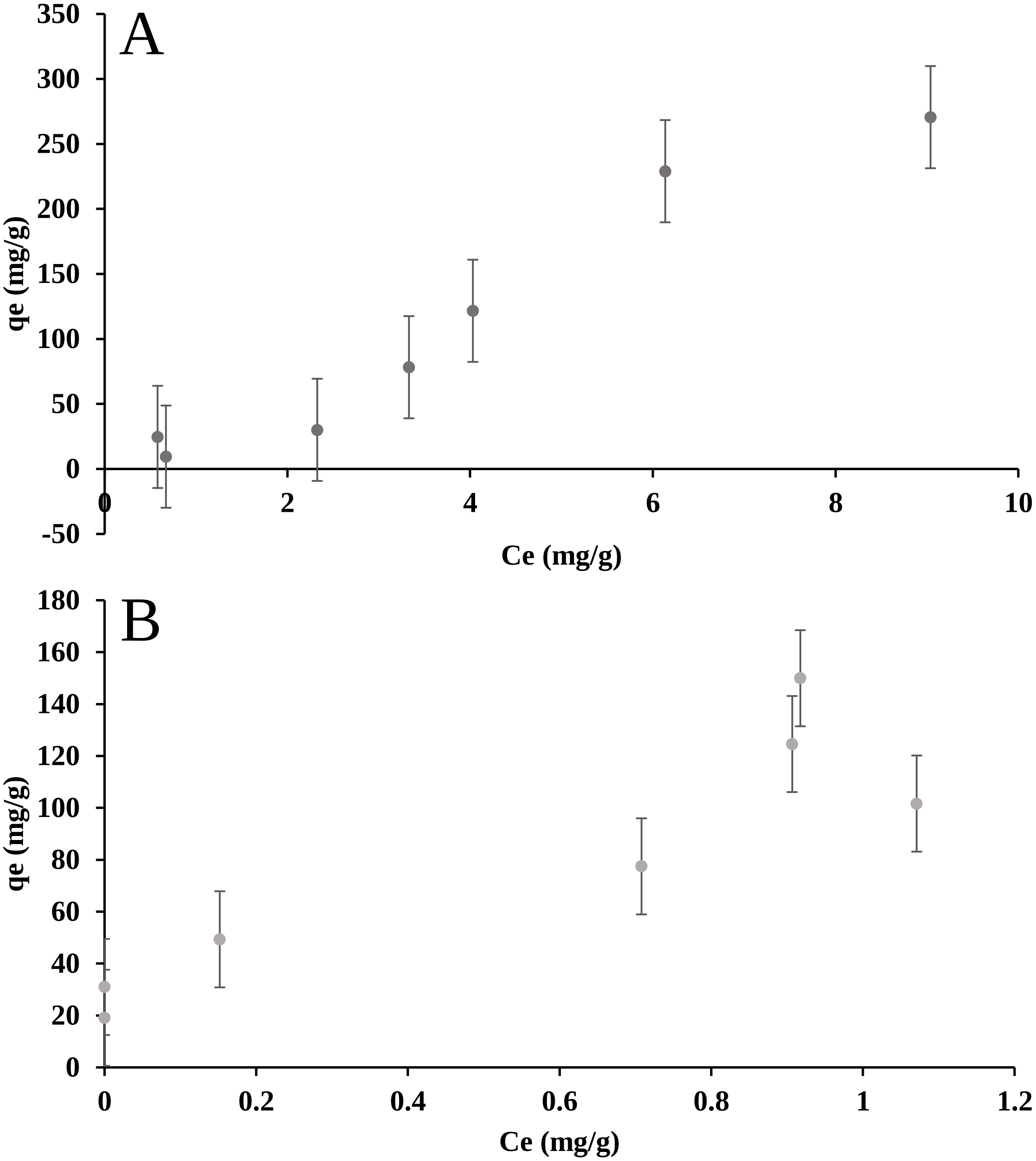

Figure 17. Adsorption capacity (mg/g) of (A) lead and (B) nickel on biochar at equilibrium concentration (mg/g) in soil.

4.5 Pot experiment

The agronomic impact of *P. juliflora* biochar on the growth of tomato plant (*Solanum lycopersicum*) grown in different pot treatments (see section 3.7) was reflected by plant height, number of leaves, chlorophyll content, and heavy metal concentrations in plants.

4.5.1 Effect of biochar on plant height. Plant heights (cm) were measured individually for all plants and under all treatments from week 1 to week 7 after the establishment stage of the experiment. The heights were measured from the surface of the soil to the upper tip of the plant. The results in Figures 18 and 19 illustrate the plant height at week 7 of the pot experiment. It can be observed from Figure 18 that the difference in plant height between treatments is not statistically significant ($p > 0.05$) level. However, Figure 19 demonstrates that the difference in plant height between treatments is statistically significant ($p \leq 0.05$), indicating that biochar application effectively increased plant height in Treatments 3B (nickel-contaminated soil with 0.05 g of biochar) and 4A (regular soil with 0.05 g of biochar) compared to Treatments 1A (negative control: regular soil without biochar) and 2B (positive control: nickel-contaminated soil without biochar). In addition, it can be revealed from Figure 19 that there is no significant difference between Treatment 3B and 4A ($p > 0.05$), but these treatments differed significantly from Treatment 1A and 2B. Furthermore, Treatments 3A (lead-contaminated soil with 0.05 g of biochar) and 4A in figures 18 and 19 showed the maximum plant height at 52.1 cm and 52.2 cm, respectively.

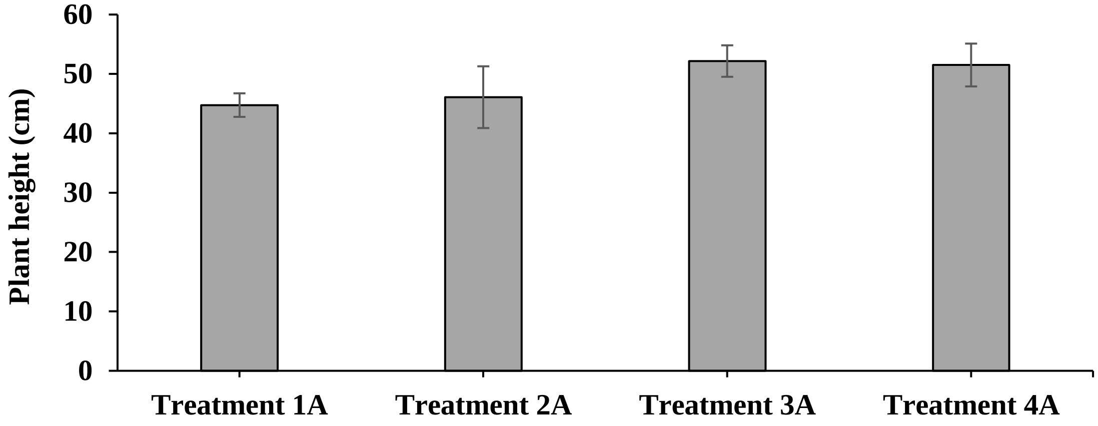

Figure 18. Plant height of tomato at different treatment levels of Treatment 1A (negative control: regular soil without biochar), Treatment 2A (positive control: lead-contaminated soil without biochar), Treatment 3A (lead-contaminated soil with 0.05 g of biochar), and Treatment 4A (regular soil with 0.05 g of biochar). Error bars refer to standard errors of the means ($n = 6$).

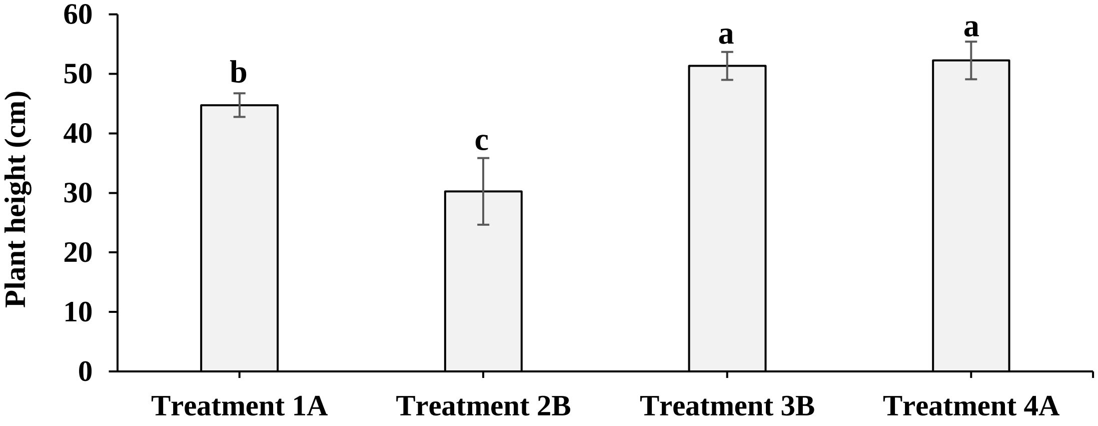

Figure 19. Plant height of tomato at different treatment levels of Treatment 1A (negative control: regular soil without biochar), Treatment 2B (positive control: nickel-contaminated soil without biochar), Treatment 3B (nickel-contaminated soil with 0.05 g of biochar), and Treatment 4A (regular soil with 0.05 g of biochar). Error bars refer to standard errors of the means ($n = 6$). Columns with the same letter are not significantly different at $p \leq 0.05$ according to Tukey's test.

4.5.2 Effect of biochar on number of leaves. The number of leaves per plant was measured during the seven weeks of the pot experiment, and the results are demonstrated in Figures 20 and 21. According to Figure 20, there was no significant difference (p > 0.05) between the treatments. However, the number of leaves in Treatments 3A and 4A was found to be higher than in Treatments 1A and 2A(positive control: lead-contaminated soil without biochar), with mean values of 96.6 and 90.5, respectively. On the other hand, Figure 21 depicts the effect of biochar on the number of leaves, which indicates that the difference between the treatments is statistically significant ($p \leq 0.05$). Where the maximum production of leaves was observed in biochar-treated soil; for Treatment 3B, it was 84.3 and for 4A, it was 90.8. These results elucidate that biochar could enhance the production of leaves in Ni-contaminated soil and regular soil.

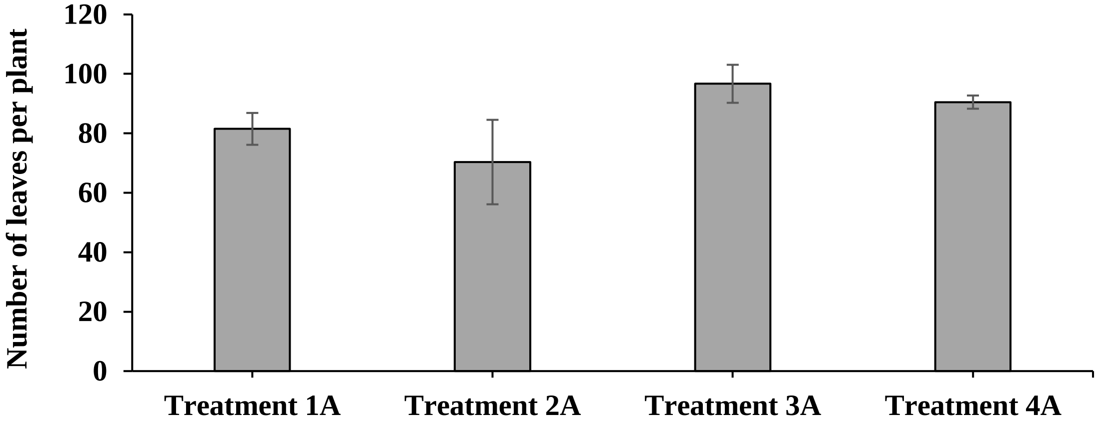

Figure 20. Number of leaves per plant at different treatment levels of Treatment 1A (negative control: regular soil without biochar), Treatment 2A (positive control: lead-contaminated soil without biochar), Treatment 3A (lead-contaminated soil with 0.05 g of biochar), and Treatment 4A (regular soil with 0.05 g of biochar). Error bars refer to standard errors of the means ($n = 6$) .

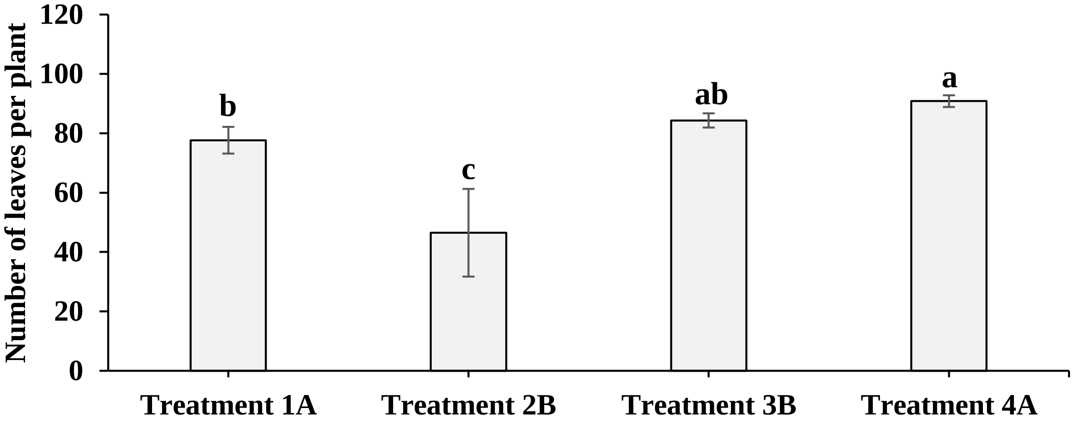

Figure 21. Number of leaves per plant at different treatment levels of Treatment 1A (negative control: regular soil without biochar), Treatment 2B (positive control: nickel-contaminated soil without biochar), Treatment 3B (nickel-contaminated soil with 0.05 g of biochar), and Treatment 4A (regular soil with 0.05 g of biochar). Error bars refer to standard errors of the means ($n = 6$). Columns with the same letter are not significantly different at $p \leq 0.05$ according to Tukey's test.

4.5.3 Effect of biochar on chlorophyll content. The measurement of chlorophyll content was undertaken at weeks 5, 6, and 7 for each treatment in order to indicate the effect of biochar on plant health. It is obvious from the obtained results in Figures 22 and 23 that treatments 3A, 3B, and 4A elucidate an increase in chlorophyll content, and this proves that biochar application potentially improves the health of the plant. However, treatments 2A and 2B showed a reduction in the chlorophyll content, and this could reflect the effect of heavy metals on the health of tomato plants. It can also be demonstrated from Figure 24, which shows the variations between the treatments and how the chlorophyll content of leaves in treated biochar treatments are obviously higher compared to Treatments 1A, 2A, and 2B.

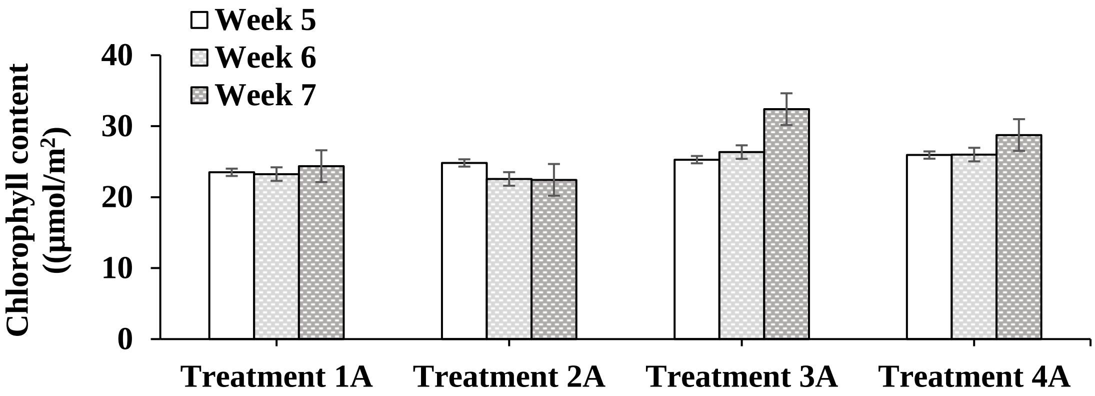

Figure 22. Chlorophyll content (µmol/m^2) in tomato plants at different treatment levels of Treatment 1A (negative control: regular soil without biochar), Treatment 2A (positive control: lead-contaminated soil without biochar), Treatment 3A (lead-contaminated soil with 0.05 g of biochar), and Treatment 4A (regular soil with 0.05 g of biochar). Error bars refer to standard errors of the mean (n = 6).

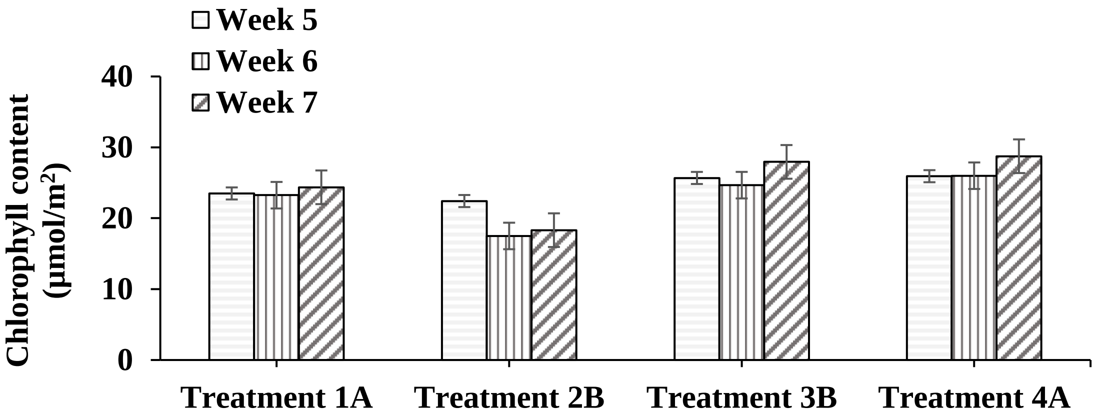

Figure 23. Chlorophyll content (µmol/m^2) in tomato plants at different treatment levels of Treatment 1A (negative control: regular soil without biochar), Treatment 2B (positive control: nickel-contaminated soil without biochar), Treatment 3B (nickel-contaminated soil with 0.05 g of biochar), and Treatment 4A (regular soil with 0.05 g of biochar). Error bars refers to standard errors of the mean ($n = 6$)

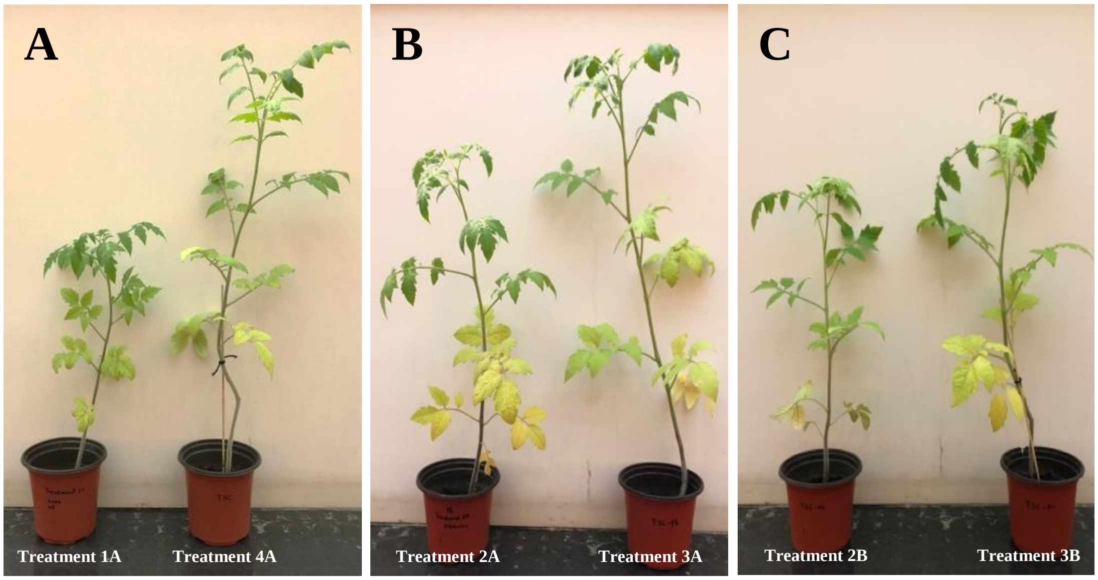

Figure 24. Variations between the pot experiment treatments **(A)** Treatment 1A (negative control: regular soil without biochar) and Treatment 4A (regular soil with 0.05 g of biochar), **(B)** Treatment 2A (positive control: lead-contaminated soil without biochar) and Treatment 3A (lead-contaminated soil with 0.05 g of biochar), and **(C)** Treatment 2B (positive control: nickel-contaminated soil without biochar) and Treatment 3B (nickel-contaminated soil with 0.05 g of biochar).

4.5.4 Heavy metal concentration on plants. The accumulation of heavy metals, specifically lead and nickel, in soil could threaten plant growth and therefore alter animal and human health. The amount of Pb and Ni accumulated in tomato tissues is shown in Figures 25 and 26, respectively.

Figure 25 highlights that lead accumulation in leaves was not significantly different ($p > 0.05$) among the treatments. In contrast, the statistical analysis revealed a significant ($p \leq 0.05$) reduction in Pb-uptake by roots under biochar-treated soil. The maximum accumulation of Pb was in Treatment 2A by 3.02 mg/Kg compared to Treatment 3A, which was amended with biochar with 1.27 mg/Kg Pb-accumulation. On the other hand, the comparison between Treatments 1A and 4A showed that biochar has effectively reduced the uptake of Pb in the roots, where the concentration of Pb in roots in Treatment 1 was 0.94 mg/Kg and in Treatment 4A it was 0.57 mg/Kg.

According to the translocation of Ni from soil to roots and leaves, a single factor ANOVA assessed that the application of biochar had a significant effect ($p \leq 0.05$) on the Ni-accumulation on roots and leaves (Figure 26). Biochar has significantly reduced the Ni concentration in both tomato roots and leaves compared to unamended treatments (Treatments 1A and 2B). Overall, the maximum accumulation of nickel was observed in Treatment 2B at 8.12 mg/kg and 7.01 mg/kg in roots and leaves, respectively. In contrast maximum reduction of Ni uptake in roots and leaves was found to be in Treatment 4A by 1.35 mg/kg and 3.37 mg/kg, respectively.

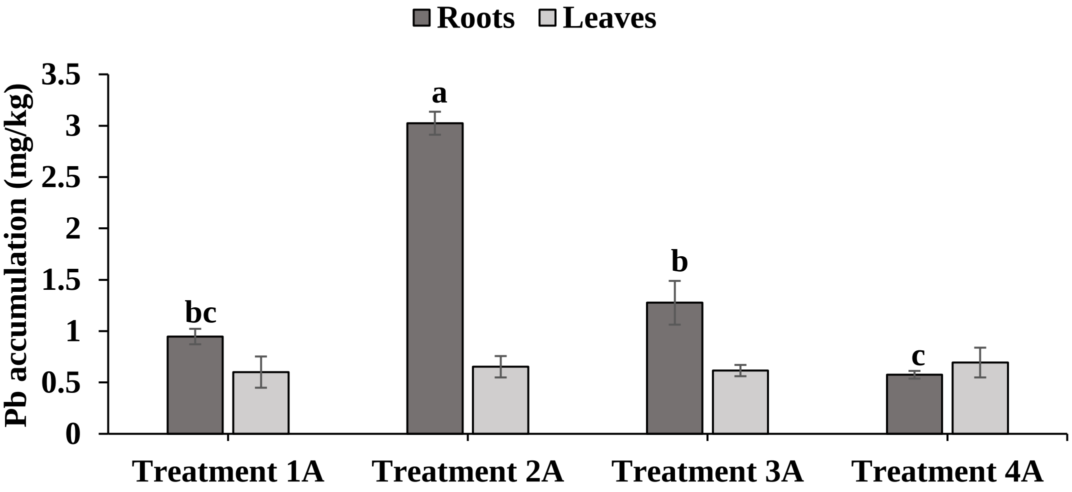

Figure 25. Pb-accumulation in roots and leaves at different treatment levels of Treatment 1A (negative control: regular soil without biochar), Treatment 2A (positive control: lead-contaminated soil without biochar), Treatment 3A (lead-contaminated soil with 0.05 g of biochar), and Treatment 4A (regular soil with 0.05 g of biochar). Error bars refer to standard errors of the means ($n = 3$). Bars with the same letter are not significantly different at $p \leq 0.05$ according to Tukey's test.

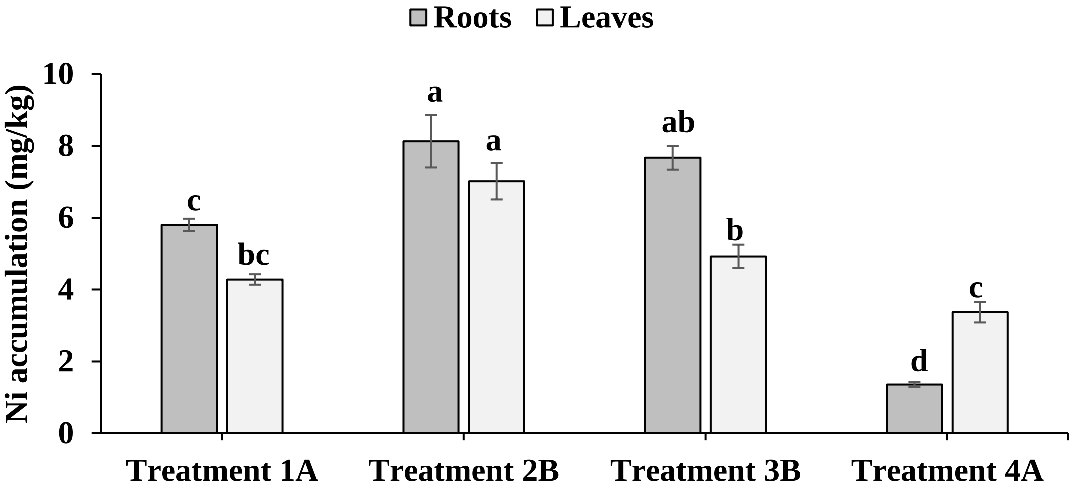

Figure 26. Ni-accumulation in leaves and roots at different treatment levels of Treatment 1A (negative control: regular soil without biochar), Treatment 2B (positive control: nickel-contaminated soil without biochar), Treatment 3B (nickel-contaminated soil with 0.05 g of biochar), and Treatment 4A (regular soil with 0.05 g of biochar). Error bars refer to standard errors of the means ($n = 3$). Bars with the same letter are not significantly different at $p \leq 0.05$ according to Tukey's test.

Chapter 5: Discussion

5.1 Surface characterization of artificial contaminated soil

Soil interactions with heavy metals can be demonstrated using different analytical methods in order to study the surface compounds and the morphology of the soil that contribute to several chemical and physical interactions. It can be challenging to comprehend and predict sorption mechanisms in soils. However, technological advancements and data analysis techniques have made it possible to develop analytical tools and methods that can distinctly measure the sorption mechanisms of heavy metals, opening up new perspectives on the mechanisms governing the chemical and physical interactions that occur in soil. Fourier transform infrared (FTIR) considers as one of the quantitative analytical methods used to study the bonding mechanisms of different molecules namely, minerals, organic and inorganic components, and metal oxides on soil surfaces (Strawn, 2021). The regions observed between 3700 cm^{-1} to 3100 cm^{-1} in Figure 8 were found to correspond to hydrogen bond (O-H) that exists in water, and hydro-silicates (Si-O-H) that indicate the presence of kaolinite, quartz, and aluminosilicates (Opeyemi Śliwińska et al., 2019; Krivoshein et al., 2022). Consistent with these findings, Xing et al., (2016) found a broad band from 3500 cm^{-1} to 3100 cm^{-1} that revealed the stretching vibrations of O-H and N-H, and these results obtained the presence of water and different organic material groups such as alcohol, phenol, and amides groups.

According to FTIR results of soil samples found by Stuart (2004) where different vibrations bands composed of oxygen were obtained which related to several functional groups namely alcohol, acetates, carbohydrates, ethers, and phenols in the region of 1400 cm^{-1} to 950 cm^{-1}. Additionally, bands attributed to the FTIR region of 1100 cm^{-1} to 900 cm^{-1} reflected the presence of silicate and phosphate (PO_4^{3-}). Furthermore, the results in Figure 7 related to the peak of 885

cm^{-1} corroborated with the findings of Robinson et al., (2015), which found a distinct peak at 874 cm^{-1} that was attributed to the presence of carbonate. In a study done by Opeyemi Śliwińska et al., (2019) where they obtained different intense peaks between 1000 cm^{-1} – 800 cm^{-1} that attributed to the stretching vibration of C-H, N-H, and O-H bonds. Moreover, the bands located between 1200 cm^{-1} to 800 cm^{-1} regions were found to correspond to the presence of minerals and organic components (Linker et al., 2005). Furthermore, carbon speciation and distribution in the soil can be studied using infrared microspectroscopy, according to Hernandez-Soriano et al., (2018), the bands in 3650 cm^{-1}, 2920 cm^{-1}, 1600 cm^{-1}, and 1035 cm^{-1}, are attributed to clay minerals, aliphatic C, aromatic C, and polysaccharide C, respectively.

On the other hand, the peak at 687 cm^{-1} indicated the presence of symmetrical bending vibration of Si-O due to the quartz component in soil which considers as a non-clay mineral (Cannane et al., 2013). Mirroring the results of Soriano-Disla et al., (2018) the wavenumbers located in the region of 680 cm^{-1} and 580 cm^{-1} are associated with iron oxides (Fe_2O_3). In addition, according to McDowell et al., (2012), the IR region between 1500 cm^{-1} and 600 cm^{-1} indicated the vibration of silicate minerals in the soil. Furthermore, regions located in wavenumbers less than 900 cm^{-1} correspond to soil minerals for instance quartz and iron oxides (Xing et al., 2019). Table 9 illustrate the investigated soil compound and band assignments of soil functional groups by FTIR recorded in different literature.

Table 9. Functional groups of soil using FTIR spectroscopy as reported in previous literature.

Compound	Vibrations	Wavenumber (cm^{-1})	References
Clay mineral Organic materials	O-H N-H	3700 - 3100	Krivoshein et al., 2022 Xing et al., 2019
Soil organic matter Silicates	C-O Si-O	2000 – 1340	Krivoshein et al., 2022
Silica (matrix II) Carbonate	O-Si-O CO_3^{2-}	1340 - 800	Krivoshein et al., 2022 Tatzber et al., 2007 Tatzber et al., 2010
Quartz (matrix I)	O-Si-O	840 - 200	Krivoshein et al., 2022 Tatzber et al., 2010

Different changes occurred in peaks intensities and positions after the addition of Pb (II) and Ni (II) into the soil that can be obtained in Figure 7, these changes indicated the ion exchange behavior between clay minerals in the soil and the cationic heavy metals, moreover, to the electrostatic interaction on the soil surface (surface bonding) (Caporale and Violante, 2016). Furthermore, the presence of aluminosilicates and phyllosilicate enhanced the strong chemical adsorption of Pb and Ni with Al-O-H and Si-O-H groups, forming inner-sphere complexes with the clay minerals, and resulted in the formation of heavy metal hydroxide precipitates (Caporale and Violante, 2016). In addition, the sorption of heavy metals on soil minerals is achieved through different processes namely adsorption followed by precipitation and transformation (Sparks et al., 2013).

Soil organic matter was found to enhance the retention of Pb (II) and Ni (II) through several mechanisms namely, surface complexation, precipitation, and ion exchange due to the variation of functional groups (Ramachandran and Souza, 2013). In addition, changes that occurred in peaks 972 cm^{-1} and 977 cm^{-1} for Pb-loaded soil and Ni-loaded soil could explain the complexation and precipitation of these heavy metals as metal phosphates (Bradl, 2004). As reported by Wuana and Okieimen, (2011), the predominant insoluble Pb compounds in soil were found to be lead carbonate ($PbCO_3$) and lead phosphate $Pb_3(PO_4)_2$. Moreover, Zhu et al., (2016) found that immobilization of nickel can be done through its precipitation with $CaCO_3$ and form $NiCO_3$ in soil. On the other hand, changes that happened in peak 885 cm^{-1} indicated the metals sorption in soil due to the presence of calcium carbonate that led to outer sphere complexation on the negative charges on the surface of the soil (Mourid, 2014). In addition, slight changes in peak 687 cm^{-1} demonstrate the binding of iron oxide compound on the soil surface with Pb and Ni, respectively (Wan et al., 2018; Shen et al., 2020). Additionally, Shi et al. (2021) found that Fe_2O_3 contains oxygen-containing ligands that allowed the adsorption of heavy metals.

Different studies revealed that soil pH plays a role in the adsorption, precipitation, and stabilization of heavy metals with the soil components such as organic matter and inorganic minerals. Ramachandran and Souza (2013) found that high pH allows the retention of heavy metals with carbonates as carbonate salts. On the contrary, at a low pH value of soil, the dominant mechanism of heavy metals retention would be the ionic exchange. Moreover, at high pH the negative charge on the colloids increases which allows the formation of heavy metal hydroxide and carbonate precipitates (Xu et al., 2021). Another reason is the presence of oxygen-containing groups that complex with heavy metal ions which in turn shifted the peaks and change their intensities (Opeyemi Śliwińska et al., 2019).

On the other hand, surface morphology analysis of soil can be done through Scanning Electron Microscopy, which gives an analysis of soil texture, pores, and occupied compounds by their structures. The Soil morphology in Figure 9 (ABC) obtained has a branch-like shape that indicates the presence of hyphae which is characterized by its filamentous body shape and forming a multilayer coverage in soil, moreover, the soil surface was found to have an abundance of needle fiber calcite observed in Figure 9 (Bindschedler et al., 2012; Schurig et al., 2013). It can be spotted from the SEM image in Figure 9C the needle fiber calcite, which is composed of calcium carbonate ($CaCO_3$) that improves the sorption of heavy metals through the mechanism of biomineralization which in turn convert them into precipitates (Dixit et al., 2015; Moghal et al., 2020). In addition, The presence of carbonates such as CO_3 and PO_4^{3-}, iron oxide, and soil minerals for instance silicate enhances the retaining and immobilization of heavy metals in soil, and this can be demonstrated from the precipitation of Pb (II) and Ni (II) in Figure 9 (DEF) and (GHI), respectively (Zeng et al., 2017; Moayedi, and Mosallanezhad, 2017; Moghal et al., 2020)

5.2 Batch experiment

The effect of initial concentration on the adsorption of lead and nickel ions by biochar can be attributed to different mechanisms that affect the removal percentage and adsorption capacity. Corroborated with the results obtained in Figures 10 and 11, a previous study investigated an increase of Ni (II) removal at a low metal concentration at 100 mg/L compared to a high metal concentration at 250 mg/L with 99.8% then 71.6% respectively (Vidhya et al., 2020). This can be attributed to several factors at low metal concentrations namely the faster mobilization of Ni (II) ions into biochar active site, and the high collision and diffusion rate between metal ions and biochar surface (Vidhya et a., 2020). In addition, Shafiq et al., (2021), studied the effect of initial concentration on the potential effectiveness of biochar produced from *Eucalyptus camdulensis* on the removal of lead (II) and nickel (II) from aqueous solution. The results illustrated that the removal percentage was negatively correlated with the initial concentration, where the removal percentage of nickel decreased from 92% to 27% with the increase of metal ions concentration from 5 to 80 mg/L, and for lead reduced from 95% to 37% as the initial concentration increase from 20 to 100 mg/L; and this occurred because of the unavailability or less availability of active sites on the adsorbent surface. Consistent with the findings of adsorption capacity illustrated in Figures 10 and 11 were found to be in line with Sekulić et al., (2018) results, where the adsorption capacity positively correlated with the increase of Pb (II) and Ni (II) initial concentration. This was attributed to the higher availability of adsorption sites at high initial concentrations. The obtained results showed that the highest adsorption capacity for lead was 131.6 mg/g and for nickel, it was 72.1 mg/g at the initial concentration of 500 mg/L. The adsorption capacity of nickel observed in Figure 11, it can be similarly related to Yang et al., (2019), findings that highlighted that the adsorption capacity of nickel increased with the Ni-initial concentration, however, no further increase was obtained above 800 mg/L. Table 10 illustrates the variation of adsorption capacities of nickel and lead using different biochar produced from several biological feedstocks.

On the other hand, Mahdi et al. (2017) studied the effect of date stone biochar on the removal of nickel from an aqueous solution. The results of the batch experiment demonstrated that with the increase of Ni (II) concentration the adsorption capacity decreased, and this indicated the saturation of biochar surface sites. In another study done by Mahdi et al. (2018) on the removal of lead using biochar derived from date seeds, the study of the effect of lead adsorption and equilibrium concentration revealed that at high Pb (II) concentration, biochar available sites become saturated compared to low Pb (II) concentration where is there an abundantly available adsorption site.

Table 10. Comparison of adsorption capacity of various biochar for nickel and lead removal from current study with the literature values.

Adsorbent	**Heavy metal**	**Adsorption capacity (mg/g)**	**Reference**
P. juliflora biochar	Pb (II)	959.9	Current study
Nitrogen-doped biochar		130.87	Jiang et al., 2022
Eucalyptus camdulensis biochar		200	Shafiq et al., 2021
Ammonia-modified coconut fiber biochar		105.54	Wu et al., 2017
Hickory chips		11.2	Ding et al., 2016
Buffalo weed biochar		333.3	Yakkala et al., 2013
P. juliflora biochar	Ni (II)	381.06	Current study
Eucalyptus camdulensis biochar		54.0	Shafiq et al., 2021
Corn cob biochar		15.40	Hu et al., 2018
Sugarcane bagasse biochar		38.15	Lyu et al., 2018
Palm seed-based biochar		28.0	Gazi et al., 2018
Wheat straw pellets biochar		22.89	Shen et al., 2017

5.3 Biochar surface characterization and heavy metal adsorption

Fourier transform infrared spectroscopy (FTIR) consider one of the analytical methods used to study the surface of biochar, where it determines the functional groups' composition of the biochar surface and identifies the potential mechanisms that resulted after the application of biochar into contaminated media such as water or soil and it is interaction with heavy metals (Bandara et al., 2020). The peak obtained in Figure 13 1617 cm $^{-1}$ is related to the stretching vibrations of C in different forms of hemicellulose and lignin functionalities namely, C=O and C=C stretching (Yan et al., 2020; Janu et al., 2021). Moreover, the peak at 1400 cm $^{-1}$ was found to be attributed to the alkanes (C-H) group (Ibrahim et al., 2021). A study done by Wang et al., (2020) illustrated that the peaks between 1000 cm $^{-1}$ and 650 cm^{-1} are assigned to the presence of benzene ring vibration on the surface of biochar. Additionally, converting organic materials into biochar through the pyrolysis process improves the formation of oxygen-containing functional groups such as carboxyl, carbonyl, hydroxyl, and phenol groups this led to the increase of cation exchange capacity (CEC) and negative charge on the surface of biochar (Gomez-Eyles et al., 2013). Furthermore, biochar feedstock composed of cellulose content enhanced the sorption mechanims of heavy metals on biochar surface due to the aromaticity and alkalinity exhibited with the presence of cellulose (Ali et al., 2020). Biochar derived from different feedstocks appear to be occupied with variations of surface functional groups and this can be demonstrated in Table 11.

The application of biochar in contaminated aqueous solutions has a detrimental effect that can be observed from the changes that occurred in the peaks intensity and positions in Figure 13 due to the different mechanisms played by biochar. Similar results were attained by Wu et al., (2019), after the biochar adsorption of Pb (II), results showed that the peak at 1626 cm^{-1} was shifted to 1580 cm^{-1} demonstrating that both C=O and C=C groups played a role in the adsorption process through various mechanisms, namely complexation, and electrostatic interaction. Moreover, the strong intensity change and disappearance in peak 1400 cm^{-1} after Ni (II) and Pb (II) adsorption respectively, might indicate that the C-H group becomes available for the formation of H-bond via two mechanisms namely surface complexes and precipitation processes (Wang et al., 2018). Liu et al., (2022) obtained a shift at a peak of 1318 cm^{-1} indicating the involvement of C-O groups in the adsorption and precipitation of Pb (II). On the other hand, the changes that happened in peak intensity at 881 cm^{-1} can be supported by different studies, according to the findings of Vidhya et al. (2020) that investigated the functional group of biochar produced from coir pith after the adsorption process of Ni (II), where the results indicated that peak 879 cm^{-1} corresponding to the presence of an alkyl group and C-H bonding. Therefore, enhances the adsorption process of Ni (II). In another study, a slight shift was obtained at peak 877 cm^{-1} after the adsorption of Ni (II) and Pb (II) onto biochar, and this elucidated that the carboxylic groups contributed to the adsorption process (Shafiq et al., 2021).

Table 11. Variation between functional groups of several biochar produced from different feedstock.

Functional group	**Wavenumber (cm^{-1})**		**References**
	Current study	**In literature**	
C=C stretching	1620	1610 - 1510	Yang et al. 2007 Popescu et al. 2007 Ray et al. 2020
Aliphatic C-H_3 deformation	1396	1399-1342	Ray et al. 2020
C-O stretching	1251 -1000	900 - 1400	Khawkomol et al. 2021
Aromatic ring C-H	866	880 - 720	Chen et al. 2012 Antonangelo et al. 2019
C-H stretching	696	900 - 675	Khawkomol et al. 2021

The formation of multi pores in biochar occurs after the pyrolysis process of raw materials, which can be clearly observed in Figure 14 (ABC), due to the pyrolysis temperature that plays a role in the dehydration and volatilization of feedstock, which in turn increases the pore opening, also, because of the breakdown of hemicellulose and cellulose structures at high temperature (Usamn et al., 2015; Liang et al., 2016; Pattnaik et al., 2018). Similar results were reported by ElDamarawy et al., (2017), where the biochar produced from sugarcane bagasse showed a highly porous structure due to the pyrolysis conditions applied in the preparation process.

Moreover, the presence of porous structure could enhance the surface area of the biochar, according to Yan et al., (2022), the BET results observed were positively linked with SEM images; where the increase of porous structure and the pyrolysis temperature from 400^{o}C to 600^{o}C, lead to the increment of the surface area from 0.62 to 1.23 m^2/g. The BET of *P. juliflora* biochar measured to be 10.51 m^2/g with 0.0054 cc/g microporous volume, which indicated high surface area with pore volumes that enhance the affinity of biochar to physically adsorbed Pb (II) and Ni (II) (Inyang et al., 2016). Furthermore, Mohanty et al., (2013) found that the creaks formation and pores production increase with the increase of pyrolysis temperature from 400 to 600^{o}C. In contrast, Mendez et al., (2013) demonstrated that the fiber content increases at a low pyrolysis temperature of 400^{o}C compared to a higher pyrolysis temperature of 600^{o}C due to the increase of volatilization of feedstock. Furthermore, according to SEM analysis done by Shafiq et al., (2021), the results demonstrated that the morphology of the biochar produced from *Eucalyptus Camdulensis* characterized with roughness surface with many pores structure, which in turn enhances the adsorption of Ni (II) and Pb (II). Additionally, the white deposition observed in Figure 14 (ABC) demonstrated the presence of carbon content (Tehreem et al., 2022).

The white precipitation of Pb (II) obtained in Figure 14 (DEF) on the biochar surface was similarly in line with results attained by Godwin, (2020) where SEM analysis indicated the precipitation of Pb (II) onto the available sites of the biochar and proved applicability of the adsorption process. In addition, Shafiq et al, (2021) obtained a deposition of small particles investigated with brighter color onto the biochar surface after the adsorption process of Ni (II) and Pb (II). Furthermore, consistent with the results of biochar SEM analysis, Sekulić et al., (2018) obtained white aggregates and changes in biochar pore structure through the morphological study which proved the adsorption and interaction of Pb (II) and Ni (II) with biochar. Moreover, Inyang et al., (2011) observed mineral crystal shape on biochar morphological images which indicated the precipitation of Pb as hydro-cerussite and cerussite (lead carbonate) minerals. Furthermore, Mosa et al., (2016) found Ni-crystals on the surface of biochar which proved that precipitation was the dominant mechanism to remove Ni from an aqueous solution. These results can be distinctly observed in Figure 14 (DEF) and (GHI) for Pb (II) and Ni (II) precipitation, respectively.

5.4 Incubation experiment

The application of biochar in heavy metal-contaminated soil and sorption ability depend on three main reasons, namely, 1) electrostatic interaction occurring between the cationic heavy metals and the negatively charged surface of the biochar, 2) ionic exchange between the cations and the ionizable protons of the biochar, and 3) the sorptive interaction, including the delocalized π-bond (Sohi et al., 2010). Moreover, the presence of several functional groups on biochar such as C=O and C=C enhances the adsorption of Pb and Ni on the surface of biochar (Gomez-Eyles et al., 2013; El-Naggar et al., 2021). In addition, the pyrolysis conditions of biochar under 500°C resulted in the formation of high dissolved organic carbon (DOC), which in turn enhanced the immobilization of heavy metals through the formation of organometallic complexes (Tsai and

Chang, 2022). Beesley et al., (2011) demonstrated that the high presence of soluble carbon after the addition of organic materials plays a role in immobilizing heavy metals in soil and promoting the solubility with DOC through co-mobilization. Therefore, the application of biochar enhances the immobilization of heavy metals, for instance, a study revealed by Uchimiya et al., (2012) demonstrated that the Pb was immobilized through the addition of biochar produced at low temperatures through the pyrolysis process in Pb-contaminated soil. Moreover, El-Naggar et al., (2021) reviewed that Ni can be adsorbed onto biochar surface through multiple mechanisms, such as electrostatic attraction between the positively charge Ni and the functional groups on the biochar surface that tends to be negatively charged.

Furthermore, Olgun et al. (2013) investigated that the adsorption capacity of metals is linked to the presence of available sites on the biochar surface (adsorbent). This can be corroborated by Cao et al. (2019) findings that illustrated the high abundance of active sites with faster adsorption of metals in the initial stage of the process, however, the active sites decrease at the equilibrium stage. Another study done by Wang et al. (2022) demonstrated the ability of biochar produced at 350 ^{o}C to adsorb lead. The results of equilibrium concentration revealed that the adsorption capacity increased with the elevation of Pb concentration at the initial stage of the batch experiment, followed by a reduction in the adsorption capacity due to the gradual saturation of biochar active sites. Thereby, the results in Figure 17 elucidate that the sites on the biochar have reached saturation at a higher equilibrium concentration of Pb (II). In contrast, biochar sites were fully occupied at a Ni (II) equilibrium concentration of 0.91mg/g, and then gradually declined due to the less availability of active sites.

The results of the percentage of stabilization efficiency of Pb (II) and Ni (II) demonstrated in Figures 15 and 16 can be reflected due to increases in the pH of the soil due to the presence of biochar that is characterized by its alkaline nature and the indirect effect on the mobility of Pb and Ni in soil (Gomez-Eyles et al., 2013). The elevation of pH alters the surface charge of soil, which becomes negatively charged, and this enhances the electrostatic binding of the positively charged Pb (II) and Ni (II) with the soil surface and the precipitation in the soil. These mechanisms improved the immobilization and decreased the bioavailability of Pb and Ni in the soil. Furthermore, in this study the Pb and Ni stabilization efficiency on the 30th day was much better than that on the 10th and 20th days, this indicates that the aging of the biochar increases the stabilization ability of metals (Wang et al., 2021).

The biogeochemical behavior and forms of Pb and Ni depend on different soil factors, such as soil pH, organic matter and mineral content, and the presence of various functional groups (Gomez-Eyles et al., 2013). Various studies revealed that the initial soil pH was regarded as the main reason behind the stabilization of heavy metals (Wang et al., 2018). According to Guo et al. (2020), the pH of the soil plays a significant role in the stabilization and adsorption of heavy metals on the surface of soil and biochar, where the acidic soil tends to cause electrostatic repulsion due to the dissociation of H^+ from the functional groups of organic matter and minerals that are considered acidic. However, the increased pH resulted in more negatively charged biochar and soil surfaces, causing the oxygen-containing functional groups to dissociate and promote the stabilization of heavy metals. Results were interpreted by Salam et al. (2018) where the stabilization of heavy metals is greatly associated with high soil pH due to the addition of alkaline materials. In addition, Uchimiya et al. (2011) investigated that biochar with high O-containing groups is more efficient in retaining heavy metals. Another study done by Bashir et al. (2018) illustrated that the addition of biochar reduced the heavy metals extracted from soil and resulted due to an increase in soil pH, which in turn enhanced the immobilization through several processes, namely adsorption, and precipitation. In contrast, the increases in the soil pH due to the addition of biochar cannot be explained only by the adsorption of heavy metals on the surface of biochar, however, heavy metals also adsorb on the soil surfaces and precipitate as insoluble species such as hydroxides, carbonates, and phosphate (Gomez-Eyles et al., 2013; Guo, Song, and Tian, 2020). A study attained by Ahmad et al., (2016) illustrated that the addition of biochar derived from soya been and pine needle led to an increase of the soil pH and Pb-immobilization in different forms namely $Pb(OH)_2$ and ($Pb_5(PO_4)_3Cl$). Similar results were assigned by Li et al., (2019) demonstrated that coconut fiber biochar immobilized Pb through the formation of Pb phosphate precipitate ($Pb_3(PO_4)_2$). Therefore, the application of biochar in the lead-contaminated soil potentially transformed Pb into carbonate ($PbCO_3$) and phosphate precipitates ($Pb_3(PO_4)_2$) this transformation reduced the bioaccessibility and solubility of the soil contaminants (Guo et al., 2020). Ippolito et al. (2017) obtained a 100% reduction in Pb bioavailability after the application of biochar derived from Lodgepole pine or tamarisk, and the reduction observed was driven by the mechanism of precipitation reactions. Furthermore, Cao et al., (2009) found that 84% of Pb (II) was precipitated in the soil as Hydroxylpyromorphite $Pb_5(PO_4)_3(OH)$ compared to 16% of Pb (II) adsorbed onto biochar surface. On the other hand, for the nickel precipitation, Boostani et al., (2020) reported that biochar significantly enhanced the stabilization of Ni due to the high presence of calcium carbonate content, which in turn promoted the precipitation process of Ni.

5.4.1 Potential mechanism of heavy metals immobilization. Consistent with the results of the incubation experiment, the governing mechanisms of the enhanced adsorption of Pb (II) and Ni (II) onto biochar are summarized in Figure 27. After the application of biochar, several changes occur in soil physicochemical properties that lead to the immobilization of heavy metals, and this can be achieved through different mechanisms namely, adsorption, ion exchange, electrostatic attraction, complexation reactions, and precipitation. All these processes lead to the alteration of heavy metals through a redistribution process that led to the change of heavy metals nature from the solution phase to the solid phase resulting in the reduction of their availability and mobility (Bolan et al., 2014). In addition, the production of biochar through the pyrolysis process increases the porosity, cation exchange capacity, and the active sites on the surface of biochar due to the presence of functional groups (Zhang et al., 2017).

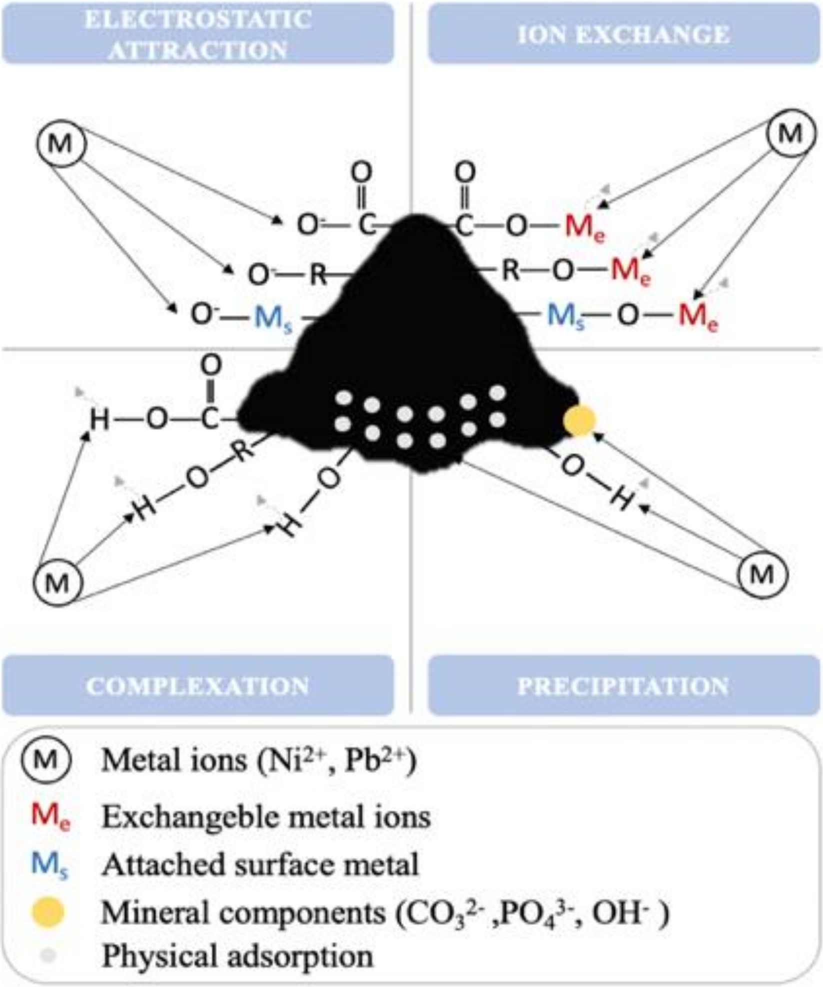

Figure 27. Illustrative diagram for the biochar mechanisms in heavy metals immobilization.

5.4.1.1 Effect of soil pH on heavy metal immobilization. The increase of soil pH after the addition of biochar leads to the immobilization of heavy metals because of the process of precipitation, reduction in metal solubility, and improves the adsorption capacity due to the increase of negatively charge on the surface of the soil (Lee et al., 2009; Houben et al., 2013). Precipitation of heavy metals in soil tends to be the predominant mechanism in high soil pH and the abundance of anions for instance carbonate (CO_3^{2-}) and phosphate (PO_4^{3-}) in highly contaminated soil (Bolan et al., 2014). In addition, the adsorption of heavy metals also occurred on the surface of biochar applied due to the increased availability of cation exchange sites with the elevation of soil pH (Harvey et al., 2011). Increases in soil pH resulted in the deprotonation of the functional groups which enhances the binding with positively charged heavy metals (Soria et al., 2020). Furthermore, Caporale and Violante (2016), found that the increment of soil pH affects the cations metal adsorption process on several charged minerals by changing the available sites of adsorption, and the concentration of different cation species such as $MeOH^+$, and Me^{2+}.

5.4.1.2 Lead (Pb) immobilization. The precipitation of Pb (II) highly depends on the carbonate buffering of biochar applied into the soil that resulted in the formation of complexes namely metal-carbonate precipitate and decreases the immobilization of heavy metals (Lee et al., 2009). Based on the study revealed by Bandara et al., (2020), biochar has the ability to precipitate Pb in different chemical reactions with PO_4^{3-} and CO_3^{2-} represented in chemical formulas (1) and (2):

$$6HPO_4^{2-} + 9Pb^{2+} + 6OH^- \rightarrow Pb_9(PO_4)_6 + 6H_2O \qquad (1)$$

$$2HCO_3^- + 3Pb^{2+} + 4OH^- \rightarrow Pb_3(CO_3)_2(OH)_2 + 2H_2O \qquad (2)$$

In addition, Fahmi et al. (2018) used plant-based biochar produced from an empty fruit bunch that formed during the production of oil palm to remediate heavy metals contaminated soil, the study demonstrated the successful role of biochar to reduces the bioavailability of Pb in the soil at high pH. Another study illustrated the formation of more stable $Pb_5(PO_4)_3(OH)$ after the conversion of less stable precipitate namely $PbCO_3$ using biochar produced from dairy manure, which in turn reduces the bioavailability of Pb (II) and enhances its stabilization in soil (Cao and Harris 2010). Similar studies indicated the formation of stable pyromorphite with low solubility (Ksp = 10^{-60}-10^{-85}) through the complexation process between Pb and phosphate; reducing its toxicity in the environment (Li et al., 2018; Shen et al., 2018). In addition, a stretching peak related to CO_3^{2-} was obtained after the application of biochar produced from wheat straw to Pb (II) contaminated soil where the results indicated the formation of $Pb_3(PO_3)_2(OH)_2$ (Shen et al., 2017).

Moreover, the presence of alkali metals namely calcium (Ca) and magnesium (mg) on the surface of the biochar can exchange easily with Pb (II), according to Ahmad et al., (2016), the cation exchange between Pb (II) with Ca (II) and Mg (II) on the surface of biochar led to the reduction of Pb (II) bioavailability and mobility, which state the negative correlation between the increases of CEC and the decreases of cation heavy metals mobility. Furthermore, the aromatic structure of biochar is characterized by the presence of π-electron on the biochar surface, leading to the electrostatic interaction (physical interaction) between the positively charged Pb (II) and the negatively charged surface of biochar, which is identified as the mechanism of cation- π bonding (Bandara et al., 2020; Soria et al., 2020). On the other hand, the abundance of O-containing functional groups on the surface of biochar enhances the removal of heavy metals and restrict their mobility in soil (Guo et al., 2020; Nkoh et al., 2021). Uchimiya et al., (2011) studied the correlation between the presence of O-containing functional groups and sorption of heavy metals on the surface of biochar produced from cottonseeds hulls. The results showed the binding of Pb (II) onto biochar surface because of the complexation process that occurred with the several functional groups namely carboxyl, hydroxyl and phenolic groups. Another factor affecting the immobilization of Pb (II) is the size of biochar, where the smaller particle size of biochar tends to provide more active sites for the Pb-mineral formation (Chen et al., 2019).

5.4.1.3 Nickel (Ni) immobilization. The possible mechanisms for Ni (II) immobilization followed a similar tendency to that of Pb (II) since it represents cationic metals. Biochar tends to lessen the mobility and bioavailability of Ni (II) in the soil through the formation of different insoluble precipitates namely with carbonate, hydroxides, and phosphate after the addition of biochar that induced such mechanism (Boostani et al., 2020; El-Naggar et al., 2021). The precipitation of Ni (II) with PO_4^{3-} can be explained by the following chemical reaction (3) and with OH^- (4) (Yang et al., 2019):

$$3Ni2+ +2(PO_4)^{3+} \rightarrow Ni_3 (PO_4)_2 \qquad (3)$$

$$Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2 \qquad (4)$$

A study conducted by Shen et al., (2017) illustrated the enhancement of soil properties after the application of biochar which in turn improves Ni (II) precipitation as Ni $(OH)_2$ and thus decreases the available concentration of Ni (II).

Furthermore, electrostatic interactions between the negatively charged functional groups on biochar and the positively charged ion of Ni are considered as a potential mechanism for Ni reduction and removal, Lyu et al. (2018) mentioned that the biochar composed of a high percentage of O-containing functional groups allowed Ni(II) to be highly adsorbed onto biochar surface physically through electrostatic interaction. In addition, El-Naggar et al., (2021) reported that Ni (II) immobilization occurs through the complexation mechanism that alters the functional groups occupied on the surface of biochar. According to a study done by Uchimiya et al., (2011), to investigate the ability of biochar derived from cottonseed hull produced at low pyrolysis temperature (350 ^{o}C) to restrict the mobility of Ni (II), the results illustrated that Ni (II) was successfully immobilized due to the presence of O-containing functional group. Another study revealed the effectiveness of plant-based biochar to adsorb Ni (II) due to the predominant abundance of hydroxyl and carboxyl groups (Alam et al., 2018). Likewise, Ali et al. (2020) determined that the oxidizable fraction of Ni (II) showed an increment after the addition of biochar to soil, and this is attributed to the mechanism of complexation reaction between Ni (II) and the surface functional groups of biochar.

On the other hand, Ni(II) was found to be exchanged ionically with several cations found on the surface of biochar, for instance, $Ca^{2+,}$ K^{+} and Mg^{2+} (Yang et al., 2019). Zhu et al., (2021) found that biochar enhanced the mechanism of ion exchange capacity through the replacement of Ni (II) with cationic ions namely sodium (Na^{+}) and calcium (Ca^{2+}), and form a complex with the functional groups of biochar.

5.5 Pot experiment

The phytoavailability of Pb and Ni in the soil is considered a concern for edible crops, which affect human health due to the inhibition of metabolic and physiological functions, which reduce plant growth and production yield (Nagajyoti et al., 2010; Alam et al., 2021; Haider et al., 2022). For instance, tomatoes that are cultivated in heavy metal-contaminated soil result in nutritional deficiency and therefore become unsuitable for human use (Khan et al., 2016; Alam et al., 2021). A remediation practice must be applied to achieve a positive effect on the cultivation of tomato plants and a maximum reduction in the mobilization and availability of heavy metals in the soil.

The results of the pot experiment in this study demonstrated that biochar prepared from *P. juliflora* has potentially improved the growth of tomato plants in heavy metal-contaminated soil.

The beneficial effects of biochar on plant height, number of leaves, chlorophyll content, and accumulation of heavy metals in plants were evaluated. The effect of biochar produced from different feedstocks on the growth of tomato plants has been examined and reported in various general studies. Suthar et al. (2018) highlighted the potential benefits of biochar derived from bamboo on the growth of tomato plants, where the pot experiment results illustrated that soil amended with biochar improved the growth and quality of tomato plants. In another study conducted by Rehman et al. (2021) on the enhancement of tomato growth under biochar-amended soil, the biochar produced from several agricultural feedstocks, namely, cotton stick, rice straw, and corncob, was applied to alkaline soil. The results proved that biochar distinctly improved the plant height, as well as the root mass and volume (Rehman et al., 2021). Additionally, Graber et al. (2010) evaluated the effectiveness of biochar produced from citrus wood on the growth of tomato plants, where the results revealed that plant heights were significantly enhanced after the application of biochar compared to the control treatment.

Consistent with the results of the effect of biochar on the plant height (section 4.5.1), a study was done by Hossain et al. (2010) to investigate the agronomic impact of biochar produced from wastewater sludge on the growth of cherry tomatoes under harsh conditions, namely, soil contaminated with heavy metals. The results obtained showed that biochar significantly increased the plant height, where the height under biochar treatment was 107.5 cm compared to control soil with 96.8 cm of plant height. Furthermore, Salam et al., (2022) examined the effect of biochar in heavy metal-contaminated soil and on plant growth parameters, and the results indicated an increment in the corn (*Zea mays*) plant height and biomass, specifically in roots and shoots.

In this regard, different studies illustrate that biochar application increases the plant height, the number of leaves, chlorophyll content, and production yield due to its impact on improving the soil properties, namely, aeration of the soil, increasing the negative charges on the soil surface, and major cations due to the increase in soil pH, which therefore increases heavy metal stabilization (Chan et al., 2007; Hossain et al., 2015; Salam, 2022; Calcan et al., 2022). In addition, biochar enhances water holding capacity and cation exchange capacity and decreases the solubility of heavy metals, which in turn provide an essential condition for the root system to grow in a healthy way. The application of biochar also improves the photosynthesis mechanism of plants, and this can be reflected by the chlorophyll content, which is considered a dependable indicator (Agegnehu et al., 2015; Hou et al., 2020). Agegnehu et al. (2016) found that chlorophyll content in wheat leaves under biochar treatment was significant, which indicates a healthier growth of wheat with the application of biochar. Moreover, Younis et al. (2016) investigated that biochar enhances the chlorophyll content of spinach plants grown in Cd-contaminated soil and that this reflected the health state of the plants.

Biochar application in heavy metal-contaminated soil has reduced the bioavailability and movement of heavy metals in soil, as well as their translocation to plants, according to different experiments conducted on different scales namely laboratory and field-scales (Kim et al., 2015; Mawof et al., 2022; Haider et al., 2022). The evaluated studies of the agronomic impact of different biochar in Pb and Ni-contaminated soil are displayed in Table 12.

Table 12. Comparison of the agronomic impact of biochar on the plants' growth under harsh environmental conditions of lead and nickel-contaminated soil from this study with the literature values.

Feedstock	**Pyrolysis temperature (ºC)**	**Contaminants**	**Plant species**	**Effects on plants**	**References**
P. juliflora	500	Pb (II)	Tomato	Reduced the Pb-uptake in root and leaves. Enhanced the plant height, number of leaves, and chlorophyll content	This study
Maize straw	550	Pb (II)	Maize (*Zea mays*)	Reduced the toxicity of Pb in maize plants, incremented in chlorophyll content and biomass dry weight of roots and shoots.	Irfan et al., 2021
Pistachio shell	350	Pb (II)	Spinach	Positively enhanced the plant height, chlorophyll content, dry weight of root and shoot, and reduced Pb-uptake in the shoot.	Turan, 2020
P. juliflora stalk	450	Pb (II)	Castor bean	Improved the plant height by 69%, chlorophyll content by 52%, and decreased the Pb-uptake in leaves.	Kiran and Prasad, 2019
Rice hull	500	Pb (II)	Lettuce (*Lactuca sative* L.)	Reduced the immobilization of Pb in soil and decreased lettuce Pb-uptake.	Kim et al., 2015

Feedstock	**Pyrolysis temperature (ºC)**	**Contaminants**	**Plant species**	**Effects on plants**	**References**
Oakwood	400	Pb (II)	Maize	Reduced the translocation of Pb in maize shoot	Almaroai et al., 2014
Giant miscanthus	600	Pb (II)	Rapeseed	Enhanced the growth of the plant with increased availability of nutrients and decreased the bioavailability of Pb in soil.	Houben et al., 2013
Rice	500	Pb (II)	Rice	Reduced the concentration of Pb in rice by 72%	Zheng et al., 2012
P. juliflora	500	Ni (II)	Tomato	Reduced the Ni-uptake significantly in root and leaves. Enhanced the plant height, number of leaves, and chlorophyll content	This study
licorice root pulp, and rice husk	350 - 550	Ni (II)	Spinach (*Spinacia oleracea*)	Reduced the uptake of Ni in plants and improved the absorption of micronutrients and plant growth.	Boostani et al., 2019
Maize	700	Ni (II)	Maize (*Zea mays*)	Decreased the translocation of Ni in roots, shoots, and leaves.	Sayyadian et al., 2019

Feedstock	**Pyrolysis temperature (ºC)**	**Contaminants**	**Plant species**	**Effects on plants**	**References**
Silver grass *Miscanthus nepalensis*	350	Ni (II)	Wheat	Enhanced the photosynthesis parameters, and grain yield, and lowered the bioavailability of Ni wheat	Shahbaz et al., 2019
Silver grass *Miscanthus nepalensis*	350	Ni (II)	Sunflower (*Helianthus annuus*) and maize (*Zea mays*)	Decreased the Ni-accumulation in roots, and shoots and enhanced the biomass yield of the grains	Shahbaz et al., 2018
Silver grass *Miscanthus nepalensis*	500	Ni (II)	Spinach (*Spinacia oleracea*)	Increased spinach biomass and decreased Ni concentration in the plant tissues.	Khan et al., 2017
Cotton sticks	450	Ni (II)	Spinach (*Spinacia oleracea*)	Improved a high chlorophyll content, and reduced the bioavailability and toxicity of Ni in roots and shoots.	Younis et al., 2015
Gliricidia sepium wood	900	Ni (II)	Tomato	Reduced the bioaccumulation of Ni in the plant and improved the dry biomass.	Herath et al., 2015

5.5.1 Effect of biochar on tomato growth under Pb-contaminated soil. Pb-contaminated soil adversely affects the growth of plants, damages plant enzymatic functions, lowers the absorption of essential nutrients, reduces the photosynthesis rate, and alters the water relationship with plants (Hadi and Aziz, 2015; Haider et al., 2022). Shahid et al. (2017) found that soil contaminated with Pb (II) has damaged the structure of the chloroplast and negatively affected the photosynthesis activity of the plant through the inhibition of stomatal systems. It also impairs the chain of electron transportation. Additionally, it was found that soybean plant leaves become thin after exposure to Pb contamination. According to the World Health Organization (WHO), the maximum Pb concentration for plants is 2 mg/kg (Ogutucu et al., 2021). Pb is translocated in the plant via the root apoplast and then restricted by two cell wall modification tissues, endodermis, and exodermis, which reduces its transport in the root and shoot; however, at high concentrations of Pb, the contaminant can reach upper parts of the plant (Collin et al., 2022). According to Nas and Ali (2018), Pb concentration in plants is reduced in the following order: roots > leaves > stem.

The application of biochar improves soil properties that in turn enhance plant growth; the increases in water holding capacity and the availability of water promote the metabolic activity followed by the biochemical compounds in plants (Zulqurnain et al., 2019). Therefore, these factors reduced the Pb toxicity to the plants. The observed findings of biochar on plant height, number of leaves, and chlorophyll content in Pb-contaminated soil were consistent with results reported by Kiran and Prasad (2019), where the pot experiment findings demonstrated that the application of biochar produced from *P. juliflora* steam has potentially enhanced the plant height and number of leaves, where biochar significantly increased plant growth parameters. In addition, *P. juliflora* biochar has a distinct effect on the chlorophyll content compared to unamended soil. Furthermore, Alam et al. (2021) elucidated that biochar significantly reduces the concentration of

Pb in tomato plants by 67.6%. Similar findings were also attained by Zulqurnain Haider et al. (2019), where the concentration of Pb found in pea plant roots decreased significantly after soil amendment with biochar, which in turn enhanced the plant height and chlorophyll content. Furthermore, Zulqurnain Haider et al. (2019) reported that the reduction of Pb was attributed to the improved properties of biochar in soil, specifically, the provision of essential nutrients for plant growth and chlorophyll content, an increase in water holding capacity, and the immobilization of Pb onto the biochar surface, resulting in an improvement of plant health associated with growth parameters.

In the current study, plants grown in soil contaminated with Pb showed reduction in plant growth parameters (Figures 18 and 20), which are mirrored by the results of Hung et al. (2014) that found a reduction in plant height and leaf number of sunflower plants. Furthermore, Pb toxicity greatly affects the photosynthesis process negatively and alters the production of chloroplast pigments. Haideret al., (2006) studied the effect of Pb contaminants on the photosynthesis process, where the results revealed an alteration in enzyme mechanisms and a reduction in the absorption of carbon dioxide, impediment of water molecules, and carbohydrate content. Furthermore, it has been reported that Pb inhibited the concentration of magnesium and iron in chlorophyll, which in turn led to chlorosis in leaves. The results illustrated in Figure 22 prove that plants grown in Pb-contaminated soil reflect lower chlorophyll content compared to those grown in amended soil with biochar (Nas and Ali, 2018). Root is considered as the main plant organ for metals uptake which depends on its structure that alters the uptake rates of the metals. The accumulation of Pb in roots and leaves differs with uptake concentrations, due to the restricted internal transport of Pb by roots which act as a barrier against the translocation of Pb to the upper part of the plant (Ifran et al., 2010; Carbonell et al., 2016; Aslam et al., 2021). In addition, a previous study demonstrated that

95% of Pb accumulates in plant roots (Chandra et al., 2018). In that case, the concentration of Pb was found to be higher at roots compared to leaves as shown in Figure 25.

5.5.2 Effect of biochar on tomato growth under Ni-contaminated soil. Nickel is an important micronutrient for the biological functions of plants; however, the elevation of Ni concentration in soil contributes to damaged plant functions and responses through the reduction of plant biomass, transpiration, and photosynthetic rate (Roccotiello et al., 2021; Haider et al., 2022). According to the WHO, the permissible limit value of Ni in plants is 10 mg/kg (Herath et al., 2015). Nickel can be diffused and transported to plants through passive and active mechanisms (Nie et al., 2015). Amari et al. (2014) investigated whether Ni (II) can adversely affect the *Brassica juncea* plants, and the results indicated that the leaves turned yellow because of the Ni alteration in the chlorophyll content. Similar results were attained by Herath et al. (2015) where the symptoms of Ni toxicity in *Lycopersicon esculentum* were diagnosed with leaf chlorosis and impediment of plant growth. In the current study, two plants from Treatment 2B were not survived and the remaining plants from the same treatment were suffered from the presence of Ni, and this can be attributed to the impact of Ni that alter the growth of tomato plants. Different symptoms were observed on the suffered plants namely, leaf chlorosis, wilted leaves, weak stem, and short in height.

The addition of biochar to Ni-contaminated soil significantly immobilizes and reduces Ni translocation in soil and plants through an adsorption mechanism on the large surface area of biochar and effectively improves soil properties, namely increasing nutrient supply to plants and water holding capacity (Khan et al., 2017). Biochar application enhances the immobilization of heavy metals, which in turn reduces their concentration in plants. The results of heavy metal accumulation in plants were corroborated by Sayyadian et al.'s (2019) findings, where the maximum concentration of Ni was observed in plants grown in unamended soil compared to soil treated with biochar, where the results obtained a reduction in Ni-uptake in plants. Furthermore, several studies confirmed the agronomic impact of biochar on the growth of plants in Ni-contaminated soil, where Herath et al., (2015) and Ramzani et al., (2017) investigated a significant reduction in Ni concentration in roots and shoots after biochar application. The possible mechanisms of biochar engaged in this reduction of Ni-uptake in plants are surface adsorption onto available functional groups of biochar; ion exchange with cations, namely, calcium, magnesium, potassium, and sodium; and physical adsorption through electrostatic attraction with the negative charges on biochar surfaces (Haiying, 2022; Khan et al., 2017). According to Shen et al. (2016), applying biochar to Ni-contaminated soil reduced its accumulation in maize due to immobilization in soil and increased competition in the root surface due to high nutrient availability in soil. Moreover, Lee et al. (2013) highlighted that biochar reduces nutrient leaching from the root zone and therefore improves nutrient levels in plants. In addition, Herath et al. (2015) found that the adsorption and diffusion of heavy metals onto biochar are based on the high surface area and pore size.

In the current study, the reduction of Ni uptake in plant roots and leaves is concomitant with the enhancement of plant growth parameters after the application of biochar, namely, plant height, number of leaves, and chlorophyll content. This is substantially observed in our findings where biochar significantly improved the plant heights, number of leaves and also increased the chlorophyll content, as shown in Figures 19, 21, and 23, respectively. Consistent with these findings, Rehman et al. (2016) ensured that plant height was significantly enhanced after the application of biochar compared to control plant samples. Furthermore, regarding the results of the effect of biochar on the chlorophyll content, Rehman et al. (2016) used biochar derived from

Eucalyptus saligna wood to reduce the accumulation of Ni in plants and enhance the growth parameters of maize. The pot experiment results revealed an increase in chlorophyll content in maize leaves due to the reduction of Ni uptake in the plant, in addition, biochar increased the essential nutrient uptake that influenced photosynthesis rate and pigment production. In contrast, plants grown in Ni-contaminated soil with no application of biochar led to the alteration of photosynthesis mechanisms and chlorophyll content (Boostani et al., 2019). Similar to previous studies, Sirhindi et al. (2015) found a reduction in chlorophyll content in tomato and soybean leaves due to the Ni-uptake in these plants. In addition, Mosa et al. (2016) studied the effects of Ni stress on tomato plants, where the obtained results illustrate a chlorosis symptom in the leaves exposed to Ni contamination due to the reduction in uptake and translocation of essential chloroplast elements, namely, iron and magnesium.

5.5.3 Biochar mechanisms to improve plant growth under heavy metal toxicity. Biochar application in heavy metal contaminated soil have a positive impact on plant growth through the improvement of several biological, chemical, and physical properties of the soil namely, increment of microbial activity and nutrients cycles increase in essential nutrients availability, enhancement soil pH, porosity, and water holding capacity (Haider et al., 2022; Haiying et al., 2022). Soil pH is considered an important factor for the availability and translocation of Pb and Ni in plants, according to Zheng et al. (2012) Pb concentration was reduced after the application of biochar due to the elevation of soil pH, which in turn increased the negative charges on the biochar surface, followed by increments in Pb adsorption capacity. On the other hand, according to Kumar et al. (2018), the uptake of Ni decreased significantly at high pH (alkaline soil). In addition, it has been demonstrated that Ni bioavailability decreased with an increase in soil pH, and this occurred because of the formation of insoluble complexes and competition with hydrogen ions (H^+) over soil sorption sites.

The responsible mechanisms of biochar that reduce the uptake of heavy metals in the plant can be summarized in the illustrative diagram in Figure 28, which illustrates the potential effects of biochar in plant growth. The immobilization of heavy metals can be achieved by biochar functional groups namely hydroxyl and carboxyl that fixed heavy metals mobility in soil and accumulation in plants by ion exchange and complexation process (Haider et al., 2022; Haiying et al., 2022). Additionally, biochar surface contains different cations namely calcium (Ca) and magnesium (Mg) therefore increasing cation exchange capacity (CEC) and decreasing the bioavailability of heavy metals. Increases in CEC led to the reduction of the solubility and leachability of heavy metals. Moreover, due to the alkalinity nature of biochar, negative charges are found to occupy the surface of biochar which in turn enhances the electrostatic attraction of positively charged metals for instance Pb^{2+} and Ni^{2+} (Haiying et al., 2022). Furthermore, due to the porous structure of biochar that ameliorates soil aeration, nutrient uptake, and microbial activities that in turn manage the mobilization of heavy metals (Mansoor et al., 2021).

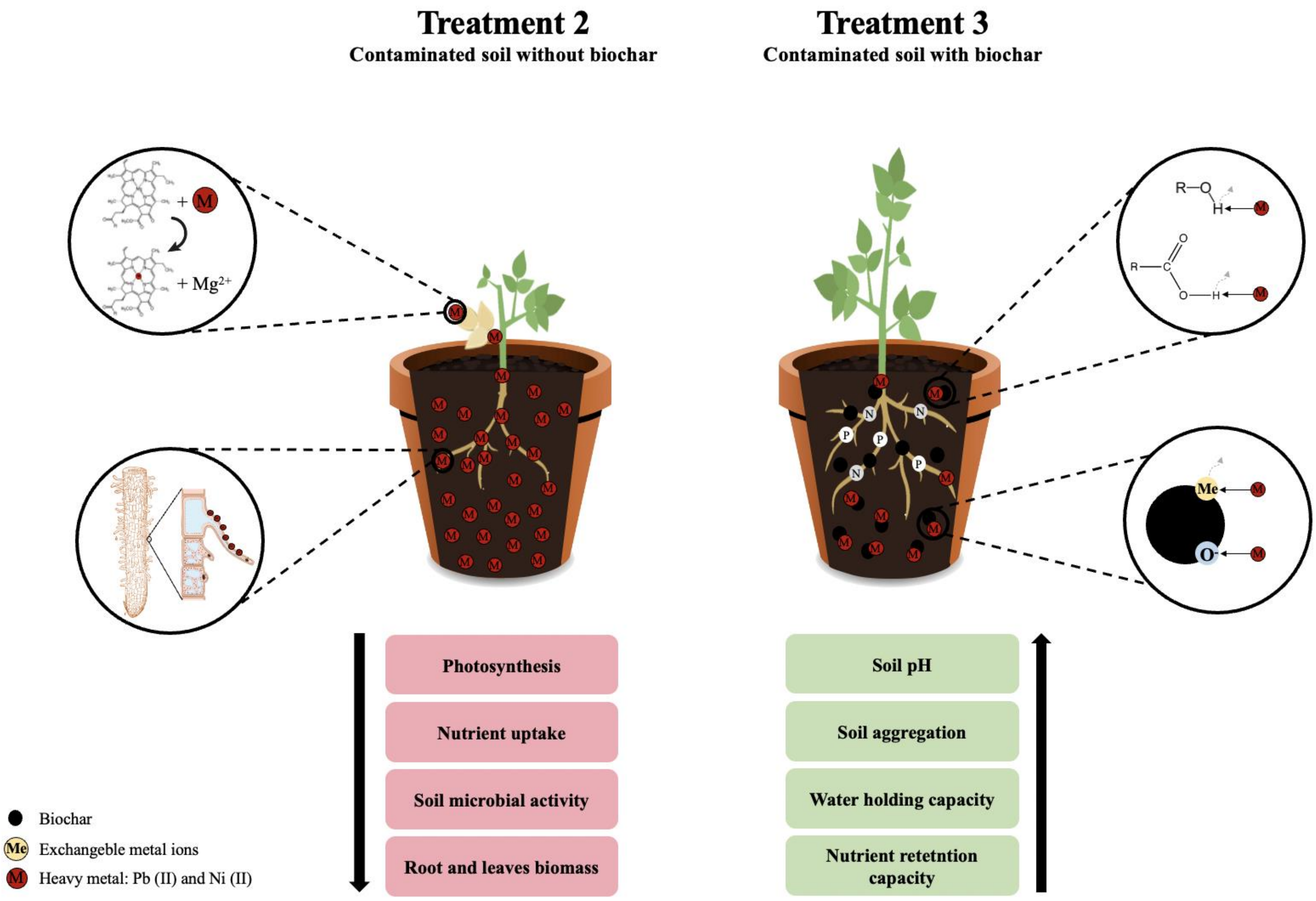

Figure 28. Illustrative diagram on the effect of heavy metals on plant growth without biochar amendment (Treatment 2) and with biochar amendment (Treatment 3)

Conclusion

The contamination of soil with heavy metals contributes to different environmental issues that negatively impact the fundamental pillars of sustainable development and agricultural and food security. In this regard, a potential remediation technology with a potential role is required to ameliorate the contaminated environment and ensure the sustainability of soil productivity and quality. Biochar is a renewable resource that serves as a valuable material converted from wastes for addressing many environmental problems, for instance, remediation of contaminants from soil. This study emphasizes the appropriate selection of biochar as a remediation technology that works in a vital way to reduce heavy metal pollution in the soil through its unique physical and chemical characteristics.

The incorporation of biochar into heavy metal-contaminated soil has the potential to reduce the concentration of heavy metals and improve soil quality and properties. Therefore, it is a dire requirement now to promote the utilization of agricultural and biological residues to produce biochar to improve the biological waste management system and beneficially enhance the soil quality for crop production and food security. According to our findings, the chemical and physical characteristics of biochar produced from *P. juliflora* were elaborated positively as a low-cost adsorbent and amendment for heavy metal removal from soil and enhancing the soil quality for agricultural purposes. In addition, a positive correlation was obtained between the adsorption capacity and initial concentrations of Pb (II) and Ni (II) that reflected the availability of active sites on the biochar surface to adsorb the contaminants both in aqueous and soil media.

The agronomic impact of biochar revealed a positive effect on the growth of tomato plants in soil amended with biochar, which reflected the potential reduction in accumulation and hazardous effect of Pb and Ni on tomato crops, and this can be attributed to the physicochemical properties of biochar associated with the prevention of mobilization and leaching of metals into the crops, therefore, enhanced the growth parameters namely, plant height, number of leaves, and chlorophyll content. Overall, the findings of this work provided insight into the potential development of a cost-effective remediation technology that contributes to reducing the negative and toxic impacts of heavy metals in soil.

Future Work

The research approach of this study has effectively answered the research questions. However, further methods and research are required to improve the application and performance of biochar for remediating contaminated soil and for agricultural purposes to ensure the production of crops of high yield and quality. In addition, expanding the application of biochar produced from biological wastes for remediating different media, such as wastewater and contaminated soil. Furthermore, combining the application of biochar with the microbial population (i.e. mycorrhizae and rhizobacteria) that exists in soil and on plants' roots to promote plant growth and the development of microbial communities. This study has examined the biochar adsorption mechanisms in aqueous media using different analytical methods. However, more research is needed on biochar modification to be easily and precisely separated from the soil in order to ensure accurate analysis. Additionally, focuses on the local economic and environmental evaluation of the biochar is required through long-term studies to obtain the maximum efficiency, viability, and accessibility of biochar application and understand their temporal variations over long periods on crop yield and soil health.

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