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The Application of Biochar for Reduction of Risk Element Availability for Cocoa (*Theobroma Cacao*) Plants

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In Prague,

....

Michael Frimpong

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Abstract

The majority of the world's cocoa is produced in Africa, with Cote d'Ivoire and Ghana making up about three-quarters of that total. Ghana has 1.7 million hectares of cocoa plantations, contributing 17% of the world's total cocoa production, second only to Cote d'Ivoire. The objective of the study was to evaluate the effect of the ability of biochar prepared from cocoa husk to decrease the mobility of heavy metals in the soil. For the biochar preparation, air-dried and fine milled cocoa bean pods were used. Pyrolysis was performed in a laboratory fixed bed reactor. Feedstock material was pyrolyzed in an electrically heated quartz tube for 30 min at the target temperatures of 400, 500, and 600 °C, respectively (labeled B400, B500, and B600), in the presence of nitrogen (nitrogen flow 3 L per minute). For comparison, a woodchips-based biochar was applied as the reference material (labeled REF). A batch sorption experiment was performed by equilibration of 0.5 g of the biochar samples with 15 ml of Cd solutions in 0.01 mol/L solution of $NaNO_3$ at 150 rpm at 25°C for 24 h. A model pot experiment was established, where cocoa (*Theobroma cacao*) seedlings were planted in the risk element polluted soil. The findings showed that the biochar prepared from cocoa husks amendments reduced the presence of cadmium in the soil. The amendments also had a significant effect on reducing the mobile concentrations of heavy metals, including Cd, Cu, Ni, Pb, and Zn, in the treated soils. The study concluded that the potential benefits of using organic amendments as a low-cost and sustainable approach to remediate heavy metal-contaminated soils.

Key Words: Biochar, Cadmium, Cocoa husk, Desorption, Heavy metals. Risk elements, Soil, Sorption, *Theobroma cacao,*

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List of the abbreviations used in the thesis

Cd = Cadmium

RE = Risk element

PAHs = Polycyclic aromatic hydrocarbons

Cu = Copper

Zn = Zinc

V = Vanadium

Ni = Nickel

W = Tungsten

Co = cobalt

Cr = Chromium

Ag = silver

As = Arsenic

Hg = Mercury

Sb = Antimony

Pb = Lead

U = Uranium

ROS = Reactive Oxygen Species

ICO = International Coffee Organization

Cl = Chloride

1. Introduction

The majority of the world's cocoa is produced in Africa, with Cote d'Ivoire and Ghana making up about three-quarters of that total (Wainaina et al. 2021). Ghana has 1.7 million hectares of cocoa plantations, contributing 17% of the world's total cocoa production, second only to Cote d'Ivoire (Isaac et al. 2020). It is a significant source of income and a vital component of Ghana's socioeconomic system. About 800,000 farmers in Ghana are directly employed by the product, and cocoa production accounts for a sizable portion of their income (roughly 80%) (Ameyaw et al. 2018). Similar to this, cocoa is the primary source of income for about 1,000,000 farmers in Cote d'Ivoire (Abdulai et al. 2018). Cocoa farming can be viewed as an agricultural production system similar to other farming systems with healthy soils paramount in contributing to high yield. According to Domagała-Światkiewicz and Siwek (2013), healthy soils produce healthy foods, which in turn contribute to human wellbeing and successful cocoa production. A soil is deemed to be in good health if it is carrying out a number of ecosystem tasks, including (1) maintaining biodiversity and animal and plant production; (2) enhancing the quality of the air and water; and (3) fostering human habitation and health. Although frequent human activity introduced pollutants like risk elements and synthetic organic compounds, it also degraded the physicochemical properties of soil. There is proof that contaminated soil prevents plant growth (Cox et al. 2001).

By stifling plant growth and weakening their resistance to pests and diseases, risk element contamination seriously jeopardizes agriculture and other sources of food for humans (Thomas et al. 2021). Cadmium is one of the main environmental pollutants (Iqbal et al. 2020). In addition to genotoxicity and oxidative stress, cadmium toxicity reduces plant uptake of mineral nutrients, gas exchange parameters, and photosynthesis (Arif et al. 2015). Agricultural and garden soils had cadmium concentrations of 0.01 to 0.7 mg kg^{-1} and 0.27 to 2.86 mg kg^{-1}, respectively (Szolnoki et al., 2013). Steps must be taken to reduce cadmium uptake from soils because cocoa (*Theobroma cacao* L) trees absorb and bioaccumulate cadmium, which can occasionally lead to unacceptable high levels of cadmium in cocoa beans (Zeng et al. 2019). According to the 2017 report by Gutiérrez E. and León C., the German Confederation of Confectioners (BDSI) contacted the Colombian Embassy in Germany to inform them of the problem of risk element residues in cocoa, particularly the presence of cadmium in imports from Latin America (Qin et al. 2018). They recommended measuring the levels of cadmium in cocoa beans and crop soils and came to the conclusion that if the levels of cadmium in the cocoa beans exceeded 0.5 mg kg^{-1}, it was wise to look into the sources of Cd in the crops and take the necessary precautions (Rizwan et al. 2016). According to the Code of Practice Concerning Source Directed Measures to Reduce Contamination of Foods with Chemicals, the advantage of removing or correcting environmental chemical contaminants at their source, including Cd in cocoa, is that the preventive approach is more effective in lowering or eliminating the risk of adverse health effects, necessitating fewer resources to control food, and preventing the rejection of food products (CXC 49-2001). As those processes cannot be "inspected" at the end of the chain, it also highlights the need for caution throughout the entire food production, processing, and distribution process (Olsen et al. 2016).

The choice of an appropriate soil ameliorant is a crucial step in the soil amendment process. Research on soil amendments has centered on biochar, which is produced by slow pyrolysis of biomass in oxygen-limited conditions (Ahmad Bhat et al. 2022). Because it typically has high carbon content and a high porosity and can be used to enhance soil structure and thereby increase plant growth, biochar has been used to amend degraded soils (Yan et al. 2021). Additionally, it increases soil carbon storage and lowers greenhouse gas emissions (Wang and Wang 2019). Previous research has shown that applying biochar to soils can immobilize risk elements (REs) and organic pollutants by altering the soil's physico-chemical properties. This is primarily due to biochar's high alkalinity, oxygenic functional groups, and hydrophobicity (Maleka 2016; Qin et al. 2018; Diquattro et al. 2020). It has been demonstrated that the leachability of contaminants in soils is primarily impacted by the sorption of REs and organic pollutants by biochar-amended soil (Gonzaga et al. 2018). Numerous studies have shown that electrostatic interaction between negatively charged functional groups and metal cations, ion exchange via proton exchange, and pore filling on the surface of biochar are among the potential sorption mechanisms of REs (Xiao et al. 2014; Rajapaksha et al. 2016; Shaheen et al. 2018, 2019). Due to the precipitation of Cd-carbonates and Pb-phosphates, some biochars added to contaminated soils improved the immobilization of Cd and Pb and decreased their bioavailability and movement to groundwater (Xu et al. 2016; Zhang and Tsang 2018). Additionally, numerous studies have shown that in soils that have been amended with biochar, the reduction in the mobility and bioavailability of REs was caused by pore diffusion, partitioning, and sorption via electrostatic interaction (Cheng et al. 2021; Li et al. 2021). Choosing the best feedstock and production method for biochar for a given use is currently the challenge; not whether biochars can be used to improve soil (Mak-Mensah et al.

2021). The objective of the study was to evaluate the effect of the ability of biochar prepared from cocoa husk to decrease the mobility of heavy metals in the soil.

2. Literature review

2.1 Soil factors affecting the soil fertility

The process of plant growth in soils is intricate. The mechanical and anchoring support of plants, nutrients and water uptake, process of producing and storing chemicals through biosynthesis, and interactions with biotic and abiotic elements of the soil are all crucial functions of roots (Pandey et al. 2001). While polluted soils, depending on limitations, impede root growth, nutrient and water uptake, and reduce plant growth, healthy soils permit roots to absorb nutrients and water, infiltrate soil particles, and ingest oxygen, allowing plants to mature to their full potential. The slow and protracted process of soil formation is influenced by the indigenous geological superficial materials over time as well as the organisms (microbes, animals, and plants) and climate, and it may also be affected by human activity (Liverpool-Tasie et al. 2016).

Soil contamination is the presence of anthropogenic chemicals in soils at levels high enough to endanger both human health and the ecosystem (Li et al. 2018). The contamination is typically brought on by commercial operations, the use of agricultural chemicals, or improper waste disposal. Polycyclic aromatic hydrocarbons (PAHs), chlorophenols, phthalates, pesticides, and heavy metals are among the most prevalent contaminants. The impact of organic substances and heavy metals in contaminated soils on plant growth and crop production, as well as the risks that go along with them, have been summarized in several recent reviews (Gruss et al. 2019).

A risk element (RE) is an inorganic chemical substance that is non-biodegradable in the environment. When present in excess in plant tissues, REs have cytotoxic, genotoxic, and mutagenic effects on plants. Some REs, including copper (Cu), zinc (Zn), vanadium (V), nickel (Ni), tungsten (W), cobalt (Co), and chromium (Cr), are trace nutrients for plants but are toxic to them when present in large quantities (Novak and Johnson 2018). Other REs, such as silver (Ag), arsenic (As), mercury (Hg), cadmium (Cd), antimony (Sb), lead (Pb), and uranium (U), have not been linked to any advantageous roles as nutrients and are, in some cases, toxic to plants even at low concentrations. Significant plant functions like photosynthesis, respiration, and enzymatic activities are negatively impacted by the increased production of reactive oxygen species (ROS) associated with elevated levels of REs (Rezaeian et al. 2020). These disturbances in homeostasis within the plant cells also result from the elevated levels of REs. Natural trace metal occurrences in the environment, especially in the crust of the Earth, contribute to the maintenance of the planet's equilibrium. Risk elements always exist at background concentration levels at their non-anthropogenic origin, where their presence in soils may be caused by parent rock weathering. Risk elements naturally occur in the ecosystem with wide variations in concentration (Awad et al. 2018).

Risk element pollution comes from a variety of sources, including metal purification. For instance, chromium and cadmium have been produced primarily as a result of the preparation of nuclear fuel, the electroplating of metals, and the smelting of copper (Nie et al. 2018). Wet and dry fallouts of atmospheric particulate matter, dead and decomposing plant and animal matter, as well as human activity, are additional sources of metal ions pollution. The mining and cement industries, smelting processes, steel mills, and burning of coal and oil are examples of anthropogenic activities that cause toxic element pollution. According to Bayuo et al. (2022), improper handling and disposal of mine drainages could lead to contamination of agricultural fields. Metal ions are released into the ecosystem through a variety of processes and pathways, including runoff into surface waters, transport into the soil and subsequently into groundwater and crops, as well as combustion emissions into the air. The presence of risk element ions in soils can be attributed to a variety of environmental factors, such as soil properties, parent materials, and human activities like farming and irrigation (Li et al. 2019). The presence of toxic metals in soil can harm crop growth and interfere with plant metabolism, major cell organelles' degeneration, and photosynthesis and respiration. In addition, the manufacture and use of synthetic products like paints, pesticides, and batteries can contaminate the environment with risk elements by contaminating agricultural soils. Risk element soil contamination is primarily brought on by the irrigation of paddy fields with wastewater from mining operations. Because of the high rate of transfer that risk elements have in soil profiles, they have the potential to contaminate groundwater. Potential metal ion accumulation and bioaccumulation in soils can seriously contaminate the food chain (Wang and Wang 2019).

Before being exposed to living organisms, risk element ions can exist for a very long time in both inorganic and organic colloids (Saltali et al. 2005). The majority of metal ions are found as microelements in humans, plants, other living things, soils, and vegetation at trace concentrations. At low concentrations, risk element traces do not kill plants or animals. There are a few exceptions, though; even in very small amounts, lead, mercury, and chromium are toxic. Food, air, and dermal contact absorption are three ways that toxic metals can enter a person's body.

They also build up in soils, plants, and aquatic biota. Metal ions may become bio-magnified when an organism expels them more slowly than it absorbs them; this can be harmful to living things. Because of the prolonged biological half-lives of risk element ions, bioaccumulation of these ions is frequently very dangerous (Guo et al. 2018).

2.2 Cadmium in the agroecosystems

As a result of human activity, such as ore processing, the burning of waste and fuels, and the use of fertilizers that contain phosphate and sewage sludge, a risk element known as cadmium is primarily released into the environment. Cadmium can also naturally enter the soil through erosive processes, volcanic eruptions, and aerosolized sea salt (Yang et al. 2021). In its most pure form, it doesn't exist in nature. Volcanic activity is the primary natural source of Cd released into the atmosphere. Sedimentary rocks and marine phosphates are two additional natural sources of this metal. It is chemically related to Zn, Fe, Pb, P, Ca, Mg, and Cu in its most common oxidation state of +2. This is due to its cation exchange ability. The concentrations of available Cd are greatly influenced by the pH of the soil, which controls its solubility and mobility. The bioavailability of the toxic risk element Cd varies depending on the properties of the soil and is persistent in the environment. Greater Cd adsorption on the surface of soil particles is preferred because it lessens this contaminant's mobility in the soil profile and, consequently, its impact on the environment. The concentration of Cd in the soil solution and, as a result, their bioavailability and mobility, are significantly regulated by the adsorption and desorption reactions on the surface of the soil colloids (Emenike et al. 2016). According to Cargua (2010), the following soil properties, including pH, texture, organic matter, Fe and Mn oxides and hydroxides, carbonates, salinity, and cation exchange capacity, can affect the accumulation and availability of risk elements. Additionally, biogeochemical processes that control cadmium mobility and availability in soil include precipitation dissolution, chelation-dissociation-complexation, mineralization-assimilation, protonation-deprotonation, metal-organic ligand formation, and redox reaction. Similar to how the type of soil, its pH, temperature, moisture content, and organic matter state, as well as by rhizosphere effects, all affect each process' relative importance.

The serious threat posed by risk element contamination of agricultural soils is to global crop production (Habiba et al., 2015). Cd is one of the risk elements that are highly toxic to plants and animals even at very low concentrations because it is not essential to living things.

Contaminated food is the main way that Cd enters humans through the food chain (Dai et al., 2012). Worldwide, cereal crops like rice, cocoa, and maize meet the majority of the food needs. More than half of the world's population relies on cocoa as their primary source of cereal, with an annual global production of about 650 million tons (FAO, 2012). When compared to other cereals, cocoa may be more likely to accumulate Cd through its roots, which may then spread to its aerial parts, which may then move into its grains (Jafarnejadi et al., 2011). Thus, the main way that humans consume Cd is through products made from cocoa. Comparing cadmium to other toxic metals like chromium, cocoa is more sensitive to cadmium (Lopez-Luna et al., 2016). The uptake and translocation of essential elements by plants, including cocoa, were inhibited by cadmium toxicity (Yourtchi and Bayat, 2013). The growth and morphology of cocoa roots are significantly impacted by Cd stress. Physiological abnormalities caused by cadmium toxicity in shoots included a decrease in photosynthesis, sugars, soluble proteins, and antioxidant enzyme activity (Li et al., 2015). Cadmium toxicity also increased the production of reactive oxygen species (ROS), which caused oxidative stress in plants (Tauqeer et al., 2016). Plant growth, biomass production, and grain yield would all be slowed by this (Ci et al., 2010a). However, the responses of various cocoa cultivars to Cd toxicity vary (Naeem et al., 2016).

Metal toxicity is primarily determined by the concentration needed to produce an acute reaction, typically a sub-lethal reaction or death. When consumed in amounts greater than those necessary for healthy growth, several trace elements are known to be toxic to people and other living things (Saltali et al. 2005). Once they enter the food chain, metal ions may have a propensity to accumulate in living tissues and, when ingested in concentrations above the legal limit, result in severe health problems. Enzymatic activities, plant development, stomatal functions, photosynthesis processes, and root system destruction have all been shown to be inhibited by risk element toxicity. Due to their fatal effects and ability to bioaccumulate through the food chain, metal ions that pollute potable water bodies pose the greatest health risks. Different metals have varying degrees of carcinogenicity, though they can also have adverse effects on the heart, hematological, gastrointestinal, neurological, musculoskeletal systems, immunological, and epidermal systems. Even at low concentrations, highly toxic metal ions have destructive impacts. Due to their potential for harm due to bioaccumulation through the food chain, risk element dangers have emerged as the most recent environmental health concern (Shaaban et al. 2018). The majority of human activities that distribute, concentrate, and chemically alter risk elements have the potential to make them more toxic. In comparison to their typical background concentrations, these activities lead to higher metal ion concentrations.

2.3 Cadmium uptake and accumulation by cocoa plants and their toxic effects

Cocoa, *Theobroma cacao*, is widely cultivated in America, Asia, and Africa. It is a crop with significant economic value since the seeds (beans) are used to produce chocolate and cocoa powder. 2012 saw a production of 4.05 million metric tonnes (ICO, 2012; Adamafio, 2013). Nigeria, behind Ghana, Cote d'Ivoire, and Indonesia, is the fourth-largest exporter of cocoa in the world. One of the primary agricultural export products of the nation is cocoa. The average annual production of cocoa beans in Nigeria between 2000 and 2010 was 389,272 tonnes. Because of the nation's limited processing capabilities, cocoa is mainly exported as beans (FAO, 2013). The husk contains significant amounts of ash (> 9%), crude fiber (> 20%), hemicellulose (11%), cellulose (35%), lignin (15%), pectin (6%), and a few minerals like potassium (3.18%), calcium (0.32%), and phosphorus (0.15%). The mesocarp contains the majority of the cellulose and crude fiber, and the endocarp has about 60% of the pectin.

Discussing the mechanisms of Cd toxicity and tolerance in cocoa as well as some potential management techniques to lessen Cd toxicity in cocoa are the objectives of the current review. Depending on the soil type, air pollution, and cocoa cultivars, cadmium uptake varies in plants (Guo et al., 2012). Dahlin et al. (2016) found that chloride (Cl^-) could mobilize naturally occurring Cd in the soil, which would increase plants' capacity to absorb it. After root uptake, the amount of Cd that is accumulated in the roots and transferred to the shoots varies depending on the plant cultivar (Adeniji et al., 2010). Some studies suggest that the higher Cd retention in roots may be caused by chelation with organic acids (Adeniji et al., 2010). While root-to-shoot Cd translocation is necessary for cadmium accumulation in plants' shoots, it can also travel directly from roots to grains through the xylem-to-phloem pathway in the stem (Harris and Taylor, 2013). Quinn et al. (2011) found that the rate of transpiration was correlated with increased shoot Cd content in plants with "low" isolines, whereas Cd accumulation was unrelated to transpiration in plants with "high" isolines.

Reduced seed germination is the first toxic effect of cadmium in cocoa, which is a highly toxic plant. The growth medium affects the toxicity of cadmium to seed germination (Ahmad et al., 2013). When growing cocoa under the same Cd levels, it has been reported that soil had better germination than filter paper, as measured by the plumule and radicle length. This may be because Cd can bind to soil exchange sites (Ahmad et al., 2013). Chlorosis, necrosis, browning of the root tips, reduced plant growth, and even plant death are the main symptoms of Cd-induced toxicity in cocoa, especially at higher Cd levels in the growth medium (Rizwan et al., 2016b). The root and shoot lengths of cocoa plants were reduced by cadmium toxicity, and the shoot length was more sensitive to cadmium stress than the root length was (Jin et al., 2015). The growth and morphology of the cocoa roots were both impacted by cadmium toxicity (Ci et al., 2010a). The number of leaves and leaf area of cocoa plants was reduced by too much Cd. The fresh and dry weights of cocoa shoots and roots were reduced due to excess Cd (Rizwan et al., 2016). Cadmium toxicity reduced the yield characteristics of cocoa, including the number, weight, and number of spikelets and grains per ear. However, the threshold of phytotoxic Cd concentrations varies depending on the genotypes of the cocoa, the dose, the length of exposure, and other elements. Chlorophyll a, Chlorophyll b, and carotenoid concentrations in cocoa leave decreased due to the presence of Cd (Chen et al., 2014). In a dose- and time-dependent manner, excessive Cd reduced the leaf's net photosynthetic rate (Pn), stomatal conductance (Gs), and transpiration rate (Tr) (Li et al., 2015). However, the characteristics of gas exchange inhibition varied between genotypes of cocoa (Shafi et al., 2011).

The growth medium's toxicity of cadmium reduced cocoa nutrition and altered nutrient ratios in the tissues of the crop (Rizwan et al., 2016b). Potassium (K), Zn, and manganese (Mn) concentrations in cocoa roots and shoots were decreased by excess Cd. Iron (Fe), magnesium (Mg), calcium (Ca), and potassium (K) concentrations in cocoa shoots were all reduced by cadmium toxicity in a dose-dependent manner (Yourtchi and Bayat, 2013). The net nitrate accumulation by cocoa plants was reduced by cadmium treatment. The Cd-mediated reduction in nutrient uptake by cocoa may be caused by Cd completing with nutrients during plant uptake at the root surface or by inhibiting the transporters/channels that load other elements into the aerial part of the cocoa. In both the shoot and the root of cocoa, cadmium toxicity reduced total soluble sugar concentrations while raising the levels of free amino acids. In summary, Cd toxicity reduced cocoa growth and biomass by impeding leaf photosynthesis, lowering gas exchange characteristics, and changing how the plant absorbed minerals and nutrients. The response of cocoa to applied Cd stress and genotypes of Cd, however, varied (Guo et al. 2018).

2.4 The role of sorbents in the reduction of risk element mobility in soil

Commercial adsorbents were previously used to remove metal ions from water but now are widely used all over the world to control soil and water contamination. The most frequently used conventional adsorbents in literature are ion exchange resins (polymeric organic resins), activated carbons, and inorganic materials such as activated silica gel, alumina, molecular sieves, and zeolites (Mees 2018). However, only four generic adsorbent types have enormous surface areas and are common in commercial markets for use for adsorption: Silica gel comes before zeolites, activated carbons, and activated alumina. The inorganic polymer known as silica gel is widely used in chromatographic columns. Silica gel is a cheap substrate for restraining different chemical functional groups. Other risk element ions and arsenic have been extracted, stabilized, and/or decontaminated from wastewater using a variety of silicate-derived gels. Silica gel was used in sequestration of several pollutants, comprising solid wastes, due to its chemical stability, endurance, and high physical strength. High arsenic detoxification was achieved by El-Moselhy et al. (2020) using silicate matrix through the development of hydrated iron oxide nanoparticles. Zhu et al. (2021) successfully used mesoporous silica materials of MCM-41 (MCM-41 is a mesoporous silica material that features a hexagonal array of cylindrical pores with a diameter ranging from approximately 1.5 to 10 nanometers) type to remove Pb(II), Cd(II), and Cu(II), from aqueous solutions

Zeolites are naturally occurring materials made of hydrated aluminosilicate with maximum cation exchangeability with metal ions. They are microporous crystal-like solids with distinct structures. Zeolite exhibits strong cation interaction and ion exchange abilities with risk element ions thanks to its highly porous structure in three-dimensional crystal lattices (Mees 2018). Zeolites are a good option for removing risk element ions because of their high porosity and sieving properties. Additionally, they have a high capacity for exchanging ions, and Ca2+, K+, and Na+ ions are among the most benign of these ions. Zeolites are becoming more and more well-known and are being used in a wide range of cutting-edge applications as a result of their rapid improvements in properties. Applications for them include radioprotection, biomedical, wastewater purification, biosensor, applied, and pure chemistry (Castro-Restrepo 2017). The surface area is unimportant when using zeolites for sorption because the process is selective and reversible. Zeolites are practically used in the fuel industries as molecular sieves, water softeners, detergent producers, and catalysts. Zeolites have been used as adsorbents to treat contaminants in water and wastewater in large quantities. Pb(II) and Hg(II) ions from aqueous media could be cleaned up using a zeolite made from fly ash. Zeolite cotton was created and prepared by Chen et al. (2021) as a type of filter for treating drinking water in homes. Additionally, zeolite composite adsorbents were used to detoxically remove both total coliforms and risk elements from wastewater. Risk element removal from water systems has been made successful with the use of high-quality type A zeolite. Additionally, it was discovered that zeolite alginate composites showed promise in the removal of Pb(II) from contaminated water solutions. For the decontamination of water containing Pb(II) and Cd(II), Makki used zeolite A4. Additionally, using Philippine natural zeolite, Pb(II), Ni(II), and Cu(II), ions from an acid mine drainage were removed (Prasad et al. 2017).

Due to its high affinity for metal ions, activated alumina is one of the most widely used adsorbents for the sequestration of risk elements. It is made of porous aluminum oxide that is resistant to abrasion and thermal stress and has a large surface area. It does not expand, contract, soften, or break down during the adsorption process (Wang and Wang 2019). Additionally, activated alumina is ideal for use in wastewater treatment because of its excellent adsorption abilities, high ion uptake capacity, cost-effectiveness, safety, and environmental friendliness. Since it has a large surface area, activated alumina is frequently used to remove fluorides, oxygenates, and mercaptans of hydrocarbons from water. The removal of As(V) from an aqueous solution using Nano alumina worked well. Novel alumina nanoparticles were also created and found to be effective at removing Ni(II) contamination from the solvent phase. In one study, Pb(II) and Cd(II) ions from aqueous media were removed using a mesoporous carbon stabilized alumina. Additionally, it has been demonstrated that an alumina composite can successfully remove Cr(VI) and methylene blue from aqueous solutions.

Black, solid carbonaceous materials with mechanical strength, high internal surface area, and porosity make up activated carbons. Activated carbon comes in a variety of forms that are used to filter contaminants out of water and wastewater, including activated carbon cloth, powdered activated carbon, and granular activated carbon. The consistent use of activated carbons in contaminant management procedures has yielded positive results. Hu et al. (2021) describe the use of activated carbon impregnated with humic acid for removing copper (II). Commercial activated carbons have many uses and a wide range of capabilities, but their high-cost places some restrictions on usage. Because of this, efforts have been made to prepare and produce affordable adsorbents using readily available, carbonaceous, and simple to activate natural materials. Organic material is thermally degraded to create activated carbon, which is then broken down into carbon granules (Lehmann et al. 2011).

Despite being widely used, commercial activated carbons are expensive adsorbents. Removing risk elements from contaminated resources has amplified interest in the development of safe, affordable, and cost-effective adsorbents that are more cost-effective than activated carbon currently on the market. Activated carbons for risk element extraction are heavily modified using natural and agricultural and industrial waste materials (Güereña et al. 2013). An efficient adsorbent should have a rapid sorption rate, broad adsorption capability, high porosity, be easy to retrieve or regenerate from water, and have a small pore diameter because adsorption capability is comparable to available surface area. These materials' typical adsorption characteristics are derived from polymer complexes with various functional groups, including simple sugars, lignin, proteins, hemicellulose, starch, and lipids. Due to their ability to combine with risk element ions to form complexes and chelates, these constituents are essential for risk element ions adsorption (Anonymous 2019). They can bind dangerous risk element ions or donate two electrons to bind hydrogen ions that are dissolved in aqueous media. Among the functional groups found in agricultural wastes are alcohols, esters, sulphydryl, amides, carboxyls, phenolics, carbonyls, and acetamids. These are the groups that have a preference for complexing with metals. Several studies have verified the presence of functional groups during adsorption experiments, as well as the capability of these groups to bind to metal ions through spectroscopy analysis. Since many local and abundantly available natural resources could be utilized as low cost biosorbents, toxic metals elimination through low-cost biosorbents is seen as cost-effective and more promising (Rhodes et al. 2008).

Nearly all tropical nations are home to the coconut palm (*Cocos nucifera* L.), a tropical oil crop, on their coasts and interiors. It is regarded by many as the "world's most useful plant" and provides raw materials, wood, and food for various handicrafts. Its widespread distribution has been aided by both its utility and capacity to adapt to various ecological situations. Coconut fruit is a staple of daily diet in many tropical nations. Over 2 million coconut trees are thought to be present on 13,615 hectares of the Nigerian coconut grove (Eziashi and Omamor, 2010). Most of the Southern states' mangrove, rainforest, and river delta regions are home to these coconut palms. Additionally, it can be found in a few remote locations up to 10^{o}N, primarily by river banks and streams. The largest coconut palm plantation can be located in Lagos State (Badagry), which is in the country of Nigeria's southwest. The husk of the coconut is made up of the exocarp and mesocarp. It is made of "coir" fibers, which have numerous industrial and domestic uses (Uwubanmwen et al., 2011). The oil that is extracted from the kernel is its main output. The husk and nut produce coconut coir, a significant fiber that is widely used in ropes, carpets, and brushes. The light, fluffy material that separates from the coconut fruit's thick mesocarp during the coir manufacturing process is known as coconut coir. It is made up of extractives like pectin and tannins, as well as cellulose and hemicellulose. After coconut is harvested, some of the fiber is frequently discarded carelessly, which causes substantial waste discarding issues in many African regions. Therefore, using it as a raw material for the creation of adsorbents will help to lessen the impact it has on the environment (Lee et al. 2017).

2.5 Factors affecting the efficiency of adsorbents in removing metal ions

Any adsorbent's selectivity determines its efficacy. Temperature, the type of adsorbate, the type of adsorbent, surface area or particle size, pH, and adsorbate concentration are just a few of the variables that can affect an adsorbent's selectivity. The process of adsorption of either metal ions or organic compounds will be influenced by the adsorbent's chemical and physical characteristics (Rajapaksha et al. 2016). The effectiveness of the adsorption process depends on the type of absorbent used. For instance, the size of the pores in activated carbons determines the size of molecules they adsorb. The application of activated carbon adsorbents is determined by the material's structure. The type of activated carbon's pore structure will have an impact on how it is used when it is developed as an adsorbent. For liquid-phase applications, mesoporous adsorbents are preferable, whereas microporous adsorbent is necessary for gas-phase applications. The surface area and bulk density of an adsorbent are additional physical characteristics that might affect its adsorption abilities. Adsorption is a phenomenon that occurs on surfaces, thus the amount of available surface space has an impact on how much adsorption occurs. The best adsorbents typically have small particle sizes and are highly porous solids (Tareq et al. 2018).

A high surface area for the adsorbent is therefore crucial for increasing the rate of adsorption. This can be accomplished by making more pores while shrinking the adsorbent into smaller sizes since smaller particle size adsorbents have mass transfer limitations and a greater decrease in internal diffusion, which makes equilibrium attainment easier and increases the likelihood that the full adsorption capacity will be reached, improving competence (Ding et al. 2010). The effectiveness of the adsorption process is also influenced by the type of adsorbate (liquid, solid, or gaseous). Any substance in liquid phase will adsorb at a slower rate than gas, frequently by a factor of 10 or more. The amount of adsorption that can happen is also significantly influenced by the adsorbate's solubility. Additionally, it has a significant impact on adsorption equilibrium. The degree of an adsorbate's adsorption and its solubility is inversely correlated (Grassi et al., 2012). The gradient in the ions' concentration in solution may have an impact on adsorption. The concentration gradient plays a role in the driving force that pushes the adsorbate toward the adsorbent surface. The availability of surface functional groups and their capacity to bind metal ions are two examples of factors that may cause the initial metal ion concentration to have an impact on the removal efficiency (especially at high concentrations) (Emenike et al. 2016).

The degree to which temperature affects adsorption depends on the surface function and structure of an adsorbent. Similarly, temperature change modifies adsorption stability in a way that depends on whether the process is exothermic or endothermic (Mohammed 2015). Adsorption is an exothermic process because it frequently involves the evolution of heat; as a result, the degree of adsorption typically reduces with rising temperature. Adsorption capacity may increase as temperature rises, according to studies that have been published. According to Shen and Duvnjak (2004), the uptake of cadmium and copper ions increases with rising temperatures. This increased level of uptake parallel to rising temperatures looks like a chemisorption mechanism (through an endothermic process). The metal ion ingestion is influenced by the adsorbent quantity in solution. Despite a decrease in the quantity adsorbed per unit mass, it is found that the measurement of adsorption efficiency rises as adsorbent dose is increased. The availability of functional group adsorption sites is theoretically expected to rise with the amount of adsorbent present. This increases the number of metal ions adsorbed, which improves the process efficiency (Fan et al. 2020).

2.6 Measures to reduce the cadmium contamination in cocoa beans

When cadmium accumulates in shoots, it may move to grains and then, as it moves up the food chain, to people and other animals. Therefore, it is essential to lower the Cd content of cocoa, especially in Cd-contaminated soils. The toxicity of Cd in cocoa has been reduced using a variety of mitigation strategies. Some examples of these methods include the use of plant growth regulators (PGRs), the appropriate application of mineral nutrients, silicon, inorganic amendments, biochar, manure, and compost (Asgher et al., 2015). Agronomic management strategies such as low-Cd-accumulating cocoa cultivars, crop rotation, planting patterns, and the application of microbes may also be used to reduce Cd uptake and toxicity in cocoa (Nie et al. 2018).

Various techniques have been used in controlling Cd toxicity in cocoa over the years. It is therefore crucial to understand where cadmium comes from and how it is distributed in the soil (Cao et al. 2020). A significant Cd augmentation of some soils used in cocoa production has been discovered in soil surveys. Topsoil has a slightly higher Cd content than subsurface soils, which may be due to soil formation methods, phosphate fertilizer addition, or industrial emissions (Zhang et al. 2018). When compared to Zn ore-type contamination, marine rock can produce Cd with a higher Cd to Zn ratio. And from these marine shale sources, it has been discovered that several regions in Latin America have significant, even extreme local Cd contamination; some Jamaican soils have higher Cd compared to Zn, which is an exceptionally uncommon occurrence. Soil samples from suspected high Cd soils should at least have their Zn and P levels checked to identify the source (Bian et al. 2014).

To reduce soil Cd availability through adsorption, activated carbon can be prepared and used using a variety of materials, preferably local (residual biomass or stubble). Activated carbon or biochar, on the other hand, are pricey soil amendments that are probably not feasible for cocoa plantations, particularly the smaller ones (Qin et al. 2018). However, it is worth noting that organic cocoa plantations shouldn't use activated carbon. There are signs that properly and consistently pruning trees can reduce the amount of Cd present in the husk. The root architecture of the cocoa tree is significantly impacted by surface pruning, which plays a major role in preventing Cd absorption, especially in volcanic soils. In addition, Zn levels in the soil should be raised when there is a deficiency. Zn and Cd are competitors, and when Zn concentration is low in the soil, Cd enters the cocoa plant and piles up in cocoa beans. Per the needs of the soil and the crop, zinc sulphate is applied annually on the cocoa farm as part of fertilization. Zinc sulfate, however, causes soil acidification, necessitating the addition of limestone (Peng and Wang 2012).

Liming is an agronomic management technique that lowers Cd amount in soils where cocoa trees are grown. Liming may also increase yield and nutrition of cocoa trees. Since the Cd content of these limes, which come from mines and are highly variable, is important to know, everything depends on where the raw materials are used to make them (Jones and Quilliam 2014). Liming on soils with pH below 5.5 is the most efficient method to date for reducing Cd bioavailability. It is important to know how to handle situations where the pH is higher than 5.5. Liming should be applied sparingly to prevent over liming. Based on experimental studies, a higher level of soil organic matter results in lower absorption of Cd and may help reduce Cd in cocoa beans. Utilizing organic fertilizers, such as compost, stabilized livestock manure, and others boost the soil's microbiological activity and organic matter content. Cadmium in cocoa beans is reduced in cocoa plantations by organic matter levels of 3 to 4% (Jeffery et al. 2017).

Using 5- to 6-year-old cocoa trees (CCN-51) in the province of Tocache, Peru, Schneider (2016) conducted a field experiment as part of her research on lime and showed that surface application of lime in cocoa plantations is feasible and can improve soil properties, even in a short amount of time. Liming enabled a rise in topsoil pH and a fall in Cd availability when compared to controls. Barraza et al. (2019) examined 29 samples of soils, soil additives, and cacao tree organs from organic farms in Ecuador that grow three different cacao cultivars as part of their first pilot study. They arrived at the subsequent conclusions: The distinct isotopic signature excludes sediments from a nearby stream, organic or mineral P fertilizers, naturally occurring or artificial atmospheric contributions, or other sources of enrichment (Ahmed et al. 2021). On the other hand, the Cd additions most likely originate from decomposing tree litter. However, more research is needed to determine whether the Cd enrichments are a result of cacao plantations recently using tree litter as fertilizer or if the Cd was naturally accumulated over a much longer period from decomposing tree material. Second, the three cacao cultivars under investigation appear to have different Cd isotope signatures in their beans. The results might suggest that the molecular mechanisms used by the National and CCN-51 cultivars (CCN-51 is a type of cocoa cultivar that was developed in the 1960s. It is a hybrid of three other cocoa varieties: Iquitos, Nanay, and Curara) for the transfer and sequestration of Cd between cacao leaves, pods, and beans are different. These results highlight the need for further, more in-depth investigation into coupled Cd isotope and concentration studies to determine whether these analyses provide useful limits for the origin, cycling, and partitioning of Cd in soil-cocoa systems and cocoa plants.

Cadmium may be present as an impurity in phosphate-type fertilizers and sedimentary phosphoric rocks. Nevertheless, since tropical soils contain low phosphorus, it is crucial to add phosphate fertilizers for successful cocoa production. However, producers must keep the amount of Cd in their phosphate fertilizers under control or adhere to any government-imposed national limits (Kotschi 2013). Additionally, using organic fertilizers can increase the phosphorus content of the soil because they have a high bioavailability of phosphorus. The potassium, phosphorus, and nitrogen ratio in fertilizers applied to cocoa crops generally vary subject to plant age and soil characteristics. Before applying, check the risk element analysis to make sure the Cd content is low. Nutrient-rich soil has a lower propensity to bioaccumulate Cd. Depending on the characteristics of the soils, soil amendments such as calcium sulfate ($CaSO_4$), cachaza (Cachaza can be used as a soil amendment due to its high content of organic matter and nutrients, When used as a soil amendment, cachaza can improve soil structure, increase water holding capacity, and enhance nutrient availability to plants), charcoal, magnesium carbonate ($MgCO_3$), zeolite, vinasse, humus, and zinc sulfate ($ZnSO_4$) can help reduce Cd levels in cocoa beans (Glaser et al. 2015). Cd flow in the soil profile can be slowed down by lime and sugarcane cake. In clay-textured soils with high sand contents, zeolite is an additional option. Additionally, using apatite (rock phosphate) to increase pH and lower soil Cd Phyto availability would be very expensive when compared to using dolomitic limestone.

2.7 Biochar and its use for soil remediation

A solid product called biochar is created when biomass is pyrolyzed or gasified in the absence or with a small amount of oxygen in a closed container (Mak-Mensah et al. 2021). High specific surface area, the presence of surface functional groups (carboxyl, hydroxyl, and phenolic), high pH, high porosity, and high nutrient content are its distinguishing features. These features may affect the hydraulic and physicochemical properties of the soil (Hussain et al. 2020). The application of biochar has the potential to significantly boost crop yields in tropical agricultural systems, research has shown. According to reports, applying biochar can improve root growth by boosting root biomass and root surface area (in some cases by more than 30%), thereby addressing plant nutrient and water deficiencies. Implementing biochar-based fertilization in smallholder cocoa (agroforestry) systems and other tropical perennial crop systems can help the world achieve several sustainable development goals (SDG), including SDGs 1, 2, 13, and 15 (no poverty, zero hunger, climate action, and life on land, respectively). This is accomplished by increasing the income and yields of farmers while also sequestering large amounts of carbon, reducing the reliance of industrial fertilizer production on fossil fuels, and improving several other ecosystem services and functions. One of biochar's main benefits is that it sequesters carbon, which is an ecosystem service that is highly valued.

The application of biochar in an iterative process has the potential to create significant carbon sinks. An innovative research area with significant potential for societal impact examines the advantages of biochar on cocoa systems. It has been demonstrated that biochar lowers the Cd bioavailability in cocoa. For farmers who grow cocoa, biochar might not be a cost-effective soil amendment because it is an expensive product. The physicochemical characteristics of risk element-polluted soil, the availability of metals (Cd), and the enzyme activities are all significantly impacted by compost, biochar, and their combinations (Xu et al. 2016). They decrease soil Cd quantity as a result. In addition, Cd mitigation could be accomplished by grafting low cadmium content cocoa plants with rootstocks to obtain new varieties that are not prone to Cd absorption and modifying soils to reduce Cd absorption by plants. Eleven cultivars of the "Chuncho" cacao variety from Cusco, Peru, ranged in Cd (mg/kg) concentration from 0.05 to 0.11, making it suitable for grafting. Furthermore, it should be advised to plant cocoa tree varieties that are less susceptible to cadmium uptake when starting new plantations (Alkharabsheh et al. 2021). The *Streptomyces* sp. strain has bioremediation potential because it inhibits cocoa plants' uptake of Cd. This has been proved through experimentation. The legumes injected with Cd-tolerant plant growth-bolstering bacteria, such as *Streptomyces* of the family Streptomycetaceae, may be helpful in biofertilization and phytoremediation of Cd-contaminated soils (Xu et al. 2016).

3. Aims of the thesis

The objective of the study was to evaluate the effect of the ability of biochar prepared from cocoa husk to decrease the mobility of heavy metals in the soil.

1. To test the sorption ability of biochar for heavy metals.
2. To test the ability of biochar prepared from cocoa husk to decrease the mobility of heavy metals in the soil.

This study hypothesized that the soil application of cocoa beans pericarp-based biochar will lead to the reduction of heavy metals uptake by cocoa plants, and, simultaneously, will enable the utilization of this waste material.

4. Materials and Methods

4.1. Biochar preparation

For the biochar preparation, air-dried and fine milled cocoa bean pods were used. Pyrolysis was performed in a laboratory fixed bed reactor using the apparatus described by Mercl et al. (2020). Feedstock material was pyrolyzed in an electrically heated quartz tube for 30 min at the target temperatures of 400, 500, and 600 °C, respectively (labeled B400, B500, and B600), in the presence of nitrogen (nitrogen flow 3 L per minute). For comparison, a woodchips-based biochar was applied as the reference material (labelled REF). Biochar (registered as a soil additive by the Central Institute for Supervising and Testing in Agriculture, CZE) was produced through gasification of wood chips in a fixed-bed multi-stage gasifier GP750 (Table 1) (Brynda et al., 2020).

Table 1. Typical range of REF biochar properties

Parameter	Unit	Typical range
Bulk density	kg/m^3	120–250
Ash, A 550°C	wt%	5–25
Volatile matter, V	wt%	3–8
Fixed carbon, FC	wt%	65–90
Lower heating value, Qi^d	MJ/kg	25–28
H/C	mol/mol	0.005–0.010
O/C	mol/mol	0.025–0.05
pH	–	11.7–12.6
Specific surface area, S_{BET}	m^2/g	350–700
Mesopore surface area, S_{meso}	m^2/g	200–350
Volume of micropores, V_{micro}	$mm^3{}_{liq}/g$	100–250
Total pore volume, V_{tot}	$mm^3{}_{liq}/g$	300–550

Source: Brynda et al. (2020)

4.2. Batch sorption/desorption experiment

A batch sorption experiment was performed by equilibration of 0.5 g of the biochar samples with 15 ml of Cd solutions in 0.01 mol/L solution of $NaNO_3$ at 150 rpm at 25°C for 24 h. The initial concentrations of Cd were: 0.5, 1, 2, 3, 5, 7.5, 10, 15, 20 mg/L. The suspensions were centrifuged for 10 min at 5400 rpm, and the supernatants were immediately analyzed. All extractions were conducted in duplicate. Inductively coupled plasma–atomic emission spectrometer (ICP-OES, Agilent 720, Agilent Technologies Inc., USA) equipped with a two-channel peristaltic pump, a Struman–Masters spray chamber, and a V-groove pneumatic nebulizer made of inert material was applied for the determination of Cd in the extracts (the experimental conditions were as follows: power of 1.2 kW, plasma flow of 15.0 l/min, auxiliary flow of 0.75 l/min, nebulizer flow of 0.9 l/min). The pH values of the individual samples (determined in background electrolyte, 0.01 mol/L $NaNO_3$, 1:30 w/v) were measured in suspension after 24 h of exposition.

The basic form of the Freundlich isotherm equation is defined in Eq. (1):

$$C_{sorb} = K_F C_{eq.}^{n} \qquad (1)$$

where C_{sorb} is the sorbed metal concentration, C_{eq} is the metal concentration in the final contact solution at equilibrium, K_F describes the partitioning between solid and liquid phases, and n describes the heterogeneity of the sorption sites.

The Langmuir isotherm equation is defined by Eq. (2):

$$C_{sorb} = \frac{S_{max} K_L C_{eq}}{1 + K_L C_{eq}} \qquad (2)$$

where K_L characterizes the bonding energy associated with an equilibrium constant, and S_{max} represents the maximum sorption capacity determined by the number of reactive surface sorption sites in an ideal monolayer system (Trakal et al., 2011; Vidal et al., 2009). The model of Bolster and Hornberger (2007) was used to evaluate non-linear isotherm parameters.

The desorption experiment was carried out where the previously element–saturated samples were dried as 35°C, and than extracted with 0.01 mol/L $NaNO_3$ (background electrolyte) for 24 h, and the concentrations of Cd in the solutions were determined by ICP-OES.

4.3. Pot experiment

A model pot experiment was established, where cocoa (*Theobroma cacao*) seedlings were planted in the risk element polluted soil. The soil originated from the vicinity of Příbram city (Central Bohemia, Czech Republic). The mining and smelting district of Příbram, Czech Republic, is known for the mining and processing of Pb-Ag-Zn polymetallic ores, which were mined from the Middle Ages until the 1970s (Ettler et al., 2007; Vaněk et al., 2005). Emissions from primary and secondary Pb smelters are responsible for high concentrations of risk elements (especially Pb, Cd, and Zn) in soils. Secondary metal processing still continues in the location, but contaminants in the emissions are effectively separated. Thus, contamination of the whole area is considered aged pollution. To guarantee the suitable growth conditions for seedlings, the polluted soil was mixed 1:1 (w/w) with a commercially available growing substrate suitable for the cultivation of the cocoa plants. The main characteristics and risk element contents in the experimental soil and in the substrate are summarized in Table 2.

Table 2. The main characteristics of the polluted soil and substrate

		Substrate	Soil
As	mg/kg	3.21 ± 0.33	54.6 ± 3.2
Be	mg/kg	0.283 ± 0.055	0.905 ± 0.014
Cd	mg/kg	0.151 ± 0.009	5.12 ± 1.89
Co	mg/kg	1.97 ± 0.23	11.3 ± 1.3
Cr	mg/kg	9.40 ± 2.71	37.3 ± 0.5
Cu	mg/kg	8.07 ± 0.30	25.2 ± 1.1
Ni	mg/kg	6.90 ± 2.21	15.8 ± 1.1
Pb	mg/kg	3.90 ± 0.60	937 ± 19
V	mg/kg	13.4 ± 1.8	59.3 ± 1.3
Zn	mg/kg	26.2 ± 0.0	218 ± 17

N	%	0.285 ± 0.007	0.165 ± 0.007
C	%	11.1 ± 0.8	1.81 ± 0.09
H	%	1.19 ± 0.12	0.366 ± 0.000
C/N ratio		37.6 ± 0.4	11.0 ± 0.1
pH		5.30 ± 0.01	5.78 ± 0.04
CEC	mmol/kg	192 ± 9.8	89.8 ± 1.5

Table 3. Experimental design of the pot experiment

Pot No.	Substrate	Soil	Biochar	Cocoa plant
1,2,3	2 kg	2 kg	None	None
4,5,6	2 kg	2 kg	80 g cocoa pods biochar B500	None
7,8,9	2 kg	2 kg	80 g Ref	None
10,11,12	2 kg	2 kg	None	Yes
13,14,15	2 kg	2 kg	80 g cocoa pods biochar B500	Yes
16,17,18	2 kg	2 kg	80 g Ref	Yes

The soil-substrate mixture was thoroughly mixed with biochar (2 % w/w) according to the experimental design presented in the Table 3. From the biochars from cocoa pods tested in the sorption/desorption experiment, the B500 biochar was chosen for comparison, the REF biochar was applied in the same rate, as well. The untreated control pots were included, as well. To evaluate the potential effect of the cocoa trees on the risk element availability, the experiment was split to two parts, i.e. pots with the same treatment and with cocoa seedlings (one seedling per pot) and without seedlings. After 4 weeks of the pot experiment duration, ca. 50g of the soil was sampled from each pot, dried at laboratory temperature, sieved, and mobile (i.e. extractable with 0.11 0.11 mol L^{-1} CH_3COOH) element contents were determined in these soils.

4.4. Analytical procedures

The pseudo-total contents of elements in the soil and substrate were determined by decomposing the samples using pressurized wet ashing (microwave-assisted wet digestion system Ethos 1, MLS, Germany) as determined by Fröhlichová et al. (2018). The proportion of bioaccessible risk element content in biochar treated soils was determined according to Quevauviller et al. (1993) by using a 0.11 mol L^{-1} CH_3COOH as an extraction agent. Each extraction was carried out in triplicate. A Hettich Universal 30 RF (Germany) centrifuge at 3000 rpm (i.e., 460 x *g*) for 10 min was used for the separation of the supernatant. The pH values of the original soils and the biochar-treated soils were determined in a 0.01 mol/L $CaCl_2$ extract (1:10 w/v). For the determination of total carbon and nitrogen in biochars, a CHNS Vario MACRO cube (Elementar Analysensysteme GmbH, Germany) analyzer was used. About 25 mg of the sample were burned in a catalytic furnace, and subsequently, C and N were determined by using a thermal conductivity detector. The cation exchange capacity (CEC) was calculated according to ISO 11260 (1994) as the sum of Ca, Mg, K, Na, Fe, Mn, and Al extractable in 0.1 mol/L $BaCl_2$ (1:10 w/v for 2 h).

4.5 Data analysis

The data collected will be analysed using data visualization and tables, this involves creating visual representations of the data such as graphs, charts, and tables to help communicate the results of the analysis. Visualizations can help to identify trends and patterns in the data that may not be apparent from descriptive statistics alone.

This is followed by data interpretation; this step involves interpreting the results of the analysis in the context of the research objectives and drawing conclusions based on the findings. Researchers may also discuss the limitations of the study and suggest areas for future research. The analysis of data on the application of biochar for reduction of risk element availability for cocoa plants would involve a combination of descriptive and inferential statistics, data visualization, and interpretation.

5. Results

5.1. Batch sorption experiment

Based on the given information, it can be observed that the sorption capacity for Cd follows the order: REF > B400 > B600 > B500 at the tested equilibrium concentrations. REF had the highest sorption capacity for Cd at all tested equilibrium concentrations, while B500 had the lowest sorption capacity. B400 had a higher sorption capacity for Cd than B600, but a lower sorption capacity than REF. B600 had a sorption capacity for Cd that was comparable to REF, but lower than REF at the highest tested equilibrium concentration. Therefore, if the goal is to maximize the sorption capacity for Cd, REF would be the most effective sorbent, followed by B400 and B600. However, if the focus is on cost-effectiveness, B600 may be a more favourable option as it has a comparable sorption capacity to REF at the tested equilibrium concentrations but may be less expensive. However, as can be seen from the course of the individual isotherms, all the tested cocoa pods-based biochars did not reach an equilibrium at the Cd concentrations used and the behavior of these materials should be tested at higher initial Cd concentrations in further research.

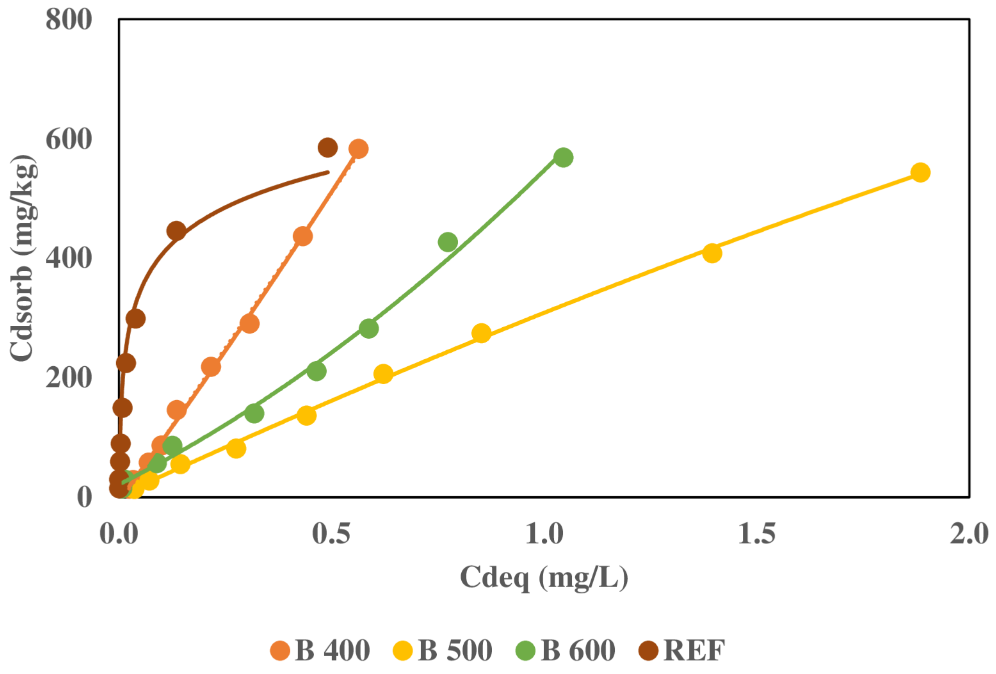

Figure 1. Sorption isotherms of Cadmium (Cd) in the individual samples

Cd_{sorb} = the content of Cd sorbed at equilibrium; Cd_{eq} = final solute Cd concentration at equilibrium

Based on the results presented in Table 4, B400, B500, B600, and REF were all tested for their ability to adsorb cadmium. The Freundlich and Langmuir equations were used to fit the sorption isotherms and determine the adsorption capacity and energy of adsorption for each sample. In terms of adsorption capacity, B400 had the highest K_F value of 1066, followed by B600 with 540.7 mmol/kg, REF with 797.1 mmol/kg, and B500 with 304.9 mmol/kg. This suggests that B400 had the highest capacity for adsorbing the tested elements, followed by B600, REF, and B500. The values of N parameter characterizing the intensity of adsorption, showed more promising results for all the cocoa pods biochars compared to the REF sample.

For the energy of adsorption, the Langmuir equation was used to determine the KL value for each sample. B500 had the highest K_L value of 0.998, followed by REF with 0.984, B600 with 0.903, and B400 with no K_L value given. This suggests that the energy of adsorption was highest in B500, followed by REF and B600, and was not determinable for B400. The results indicate that the B400 sample do not fit to the Langmuir model. The S_{max} value, which indicates the maximum adsorption capacity, was also determined using the Langmuir equation. B500 had the highest S_{max} value of 2415 mmol/kg, followed by B600 with 879.0 mmol/kg, REF with 585.9 mmol/kg.

B400 had the highest adsorption capacity, but the energy of adsorption and maximum adsorption capacity were higher in REF and B500, respectively. B600 had a higher adsorption capacity than REF, but a lower energy of adsorption. It is important to note that other factors may also influence the adsorption behaviour, such as the composition and structure of the adsorbent and the properties of the tested elements. The S_{max} value was chosen as a priority criterion for the selection of the biochar for the following pot experiment. According to the data in the Table 4, B500 was used for the pot experiment investigating the biochar sorption ability in the risk element polluted soil.

Table 4. Parameters derived from the fitting of the sorption isotherms of elements with the Freundlich and Langmuir equations

	Freundlich			Langmuir		
	E	K_F	N	E	K_L	S_{max} (mmol/kg)
B400	0.998	1066	1.06	-	-	-
B500	0.998	304.9	0.913	0.998	0.146	2415
B600	0.988	540.7	1.11	0.903	0.994	879.0
REF	0.960	797.1	0.348	0.984	33.31	585.9

Keys, E = correlation coefficient, K_F = Freundlich constant, N = parameter related to the intensity of adsorption in the Freundlich equation, KL = Langmuir constant, and Smax = maximum adsorption capacity in the Langmuir equation for the different elements (B400, B500, B600, and REF) tested.

5.3. Desorption experiment

From the Figure 2 compares the results of Cd desorption for B400, B500, B600, and REF at different initial concentrations of Cd. At all initial concentrations tested, B400 and B500 had higher amounts of Cd desorbed compared to REF. B400 showed a higher desorption capacity than

REF, especially at higher initial concentrations of Cd. B500 had a higher capacity for Cd desorption than REF for all tested Cd concentrations, while B600 had a lower capacity for Cd desorption compared to REF.

Table 5 shows that the differences in Cd desorption capacity among B400, B500, B600, and REF could be due to the specific properties of the adsorbents used, such as surface area, pore size, and chemical composition. It's also possible that the experimental conditions used, such as the pH and the presence of NaNO3, may have affected the results. The results suggest that the choice of adsorbent is important in determining the effectiveness of Cd removal, and that different adsorbents may have different capacities for Cd desorption depending on their properties and the experimental conditions used. To summarize the results, however, all the tested biochars showed excellent stability of the sorbed cadmium, because the percentage of the desorbed element did not exceed 5 % of the total adsorbed Cd regardless of the initial Cd concentration

It can observe that B500 has the highest mean desorption rate, indicating that it has the highest desorption capacity among the variables.

The p-values shows that there is a statistically significant difference between the desorption rates of B500 and the other variables, as its p-value is less than the significance level of 0.05. However, there is no statistically significant difference between the desorption rates of B400, B600, and REF, as their p-values are greater than 0.05.

Table 5: ANOVA for Cd desorption capacity among B400, B500, B600, and REF

Treatments	**Mean**	**standard deviation**	**p-value**
B400	1.60	0.32	0.105
B500	3.09	0.70	0.0001
B600	0.65	0.88	0.526
REF	0.24	0.19	0.307

$P > 0.05$

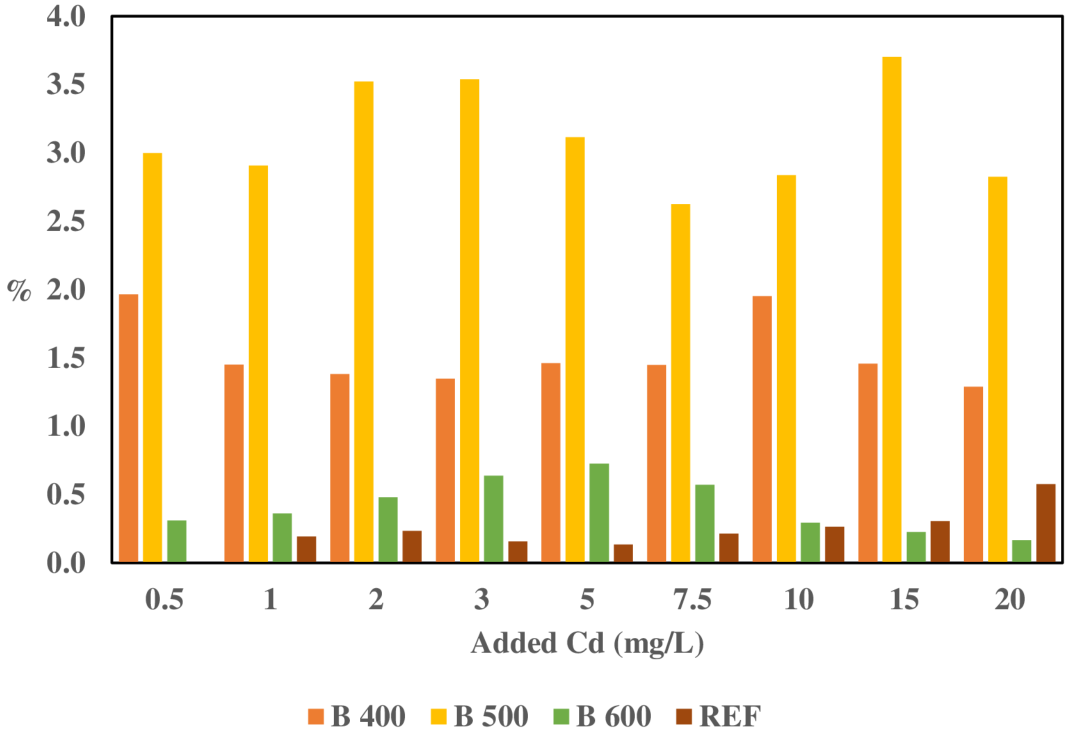

Figure 2. Desorption of Cd by using 0.01 mol/l $NaNO_3$ (background electrolyte) for the individual Cd concentrations

5.4. pH Analysis of the biochars

The results from the Figure 3 shows the differences in the solution pH after equilibration of B400, B500, B600 and REF samples. The results showed that the pH of the cocoa pods-based biochar increased with the increasing pyrolysis temperature. Except B400, the pH of the individual cocoa pods based biochars exceeded the REF sample. Whereas the pH values of the REF sample decreased with increasing Cd concentration in the equilibration solutions, the pH values of the B400, B500, and B600 samples remained almost unchanged with the increasing Cd concentration, We can spexulate that the cocoa pods biochars should have better buffering ability than the woodchips biochar REF. It is important to note that other factors, such as the experimental conditions and the specific properties of the adsorbent material, may also influence the sorption and desorption behaviour of Cd onto the samples. However, because of the importance of pH value in the Cd fate in the soils, the cocoa pods biochars seemed to be more suitable for the Cd immobilization in the soils compared to the woody biochar REF.

There is a significant difference among the variables based on the results of the ANOVA test. The p-value for each variable is less than the significance level of 0.05, indicating that there is a significant difference between each variable and the REF variable.

Table 6: ANOVA for Cd desorption capacity among B400, B500, B600, and REF

Treatments	Mean	standard deviation	p-value
B400	9.146	0.2162363289	0.0000000000326
B500	10.516	0.0412539743	0.00000000315
B600	12.225	0.0180277564	0.0000000000000000001
REF	9.26167	0.6611559695	

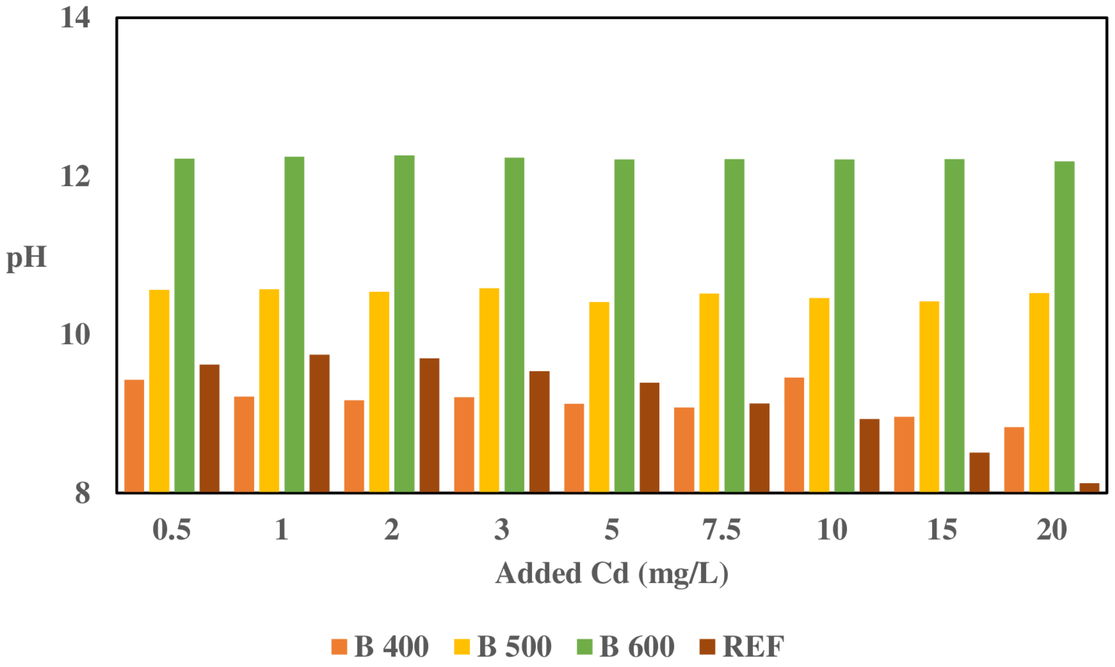

Figure 3. The pH values of the equilibrated solutions (0.01 mol/l $NaNO_3$ as background electrolyte) for the individual Cd concentrations

5.5 Pot Experiment

5.5.1. Soil pH

The results from the Figure 4 shows the results of the control, B500, and REF samples, it be observed that the presence of plants in the samples (B500 and REF) has an impact on the pH levels, as they are lower than the pH values of the control sample without plants. However, the treatment with B500 and REF did not have a significant impact on the pH levels of the soil compared to the control soil with plants.

The pH values of the samples with plants (B500 and REF) ranged from 5.20 to 5.80, with a gradual increase in pH as the samples moved towards a pH of 6.00. On the other hand, the pH values of the treated soils with plants (B500 and REF) ranged from 5.64 to 5.68, with little variation between the samples. Evidently, the one-month duration of the experiment was insufficient for the potential biochar-derived changes of pH levels in the treated soils.

From the Table 5, the p-value for the ANOVA is 0.089, which is greater than the chosen level of significance of 0.05. This suggests that there is not a significant difference in pH values between the treatments, at least at the 0.05 level of significance.

Table 7. ANOVA of pH values across Multiple Treatments

pH	Mean	standard deviation	p-value
Treatments	5.725	0.113	0.089

level of significance of 0.05

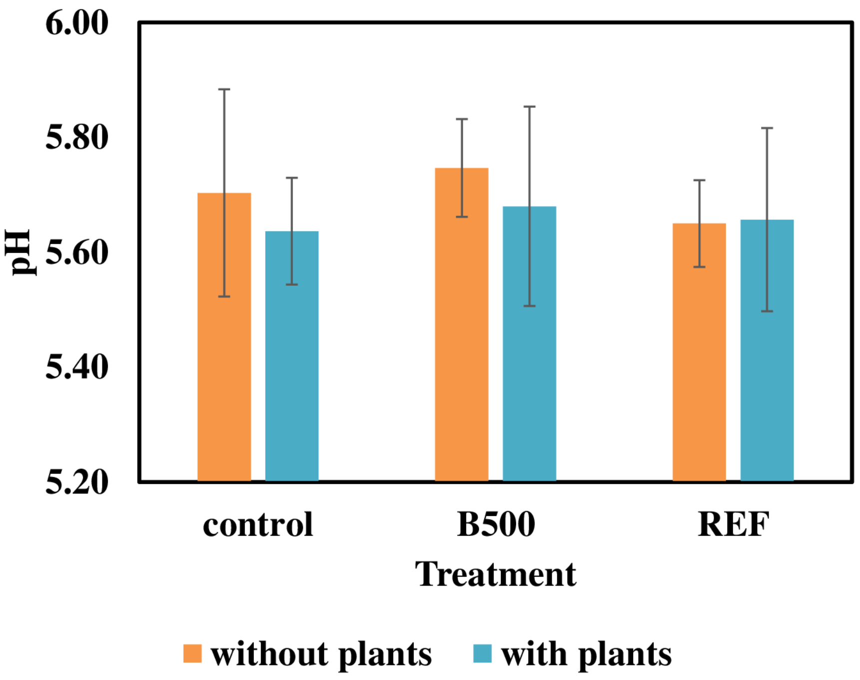

Figure 4. The pH levels of the treated soils 4 weeks after establishment of the experiment

5.5.2. Determination of Arsenic (As) content

The results reveal that the mobile contents in the treated soils without plants (B500 and REF) are slightly higher than the control soil without plants. The mobile contents in the treated soils without plants range from 1.70 to 2.0, with the highest value found in the REF sample. The treatments with B500 and REF may have had some impact on the mobile content in the soil.

The mobile contents in the treated soils with plants (B500 and REF) are slightly higher than the control soil with plants. The mobile contents in the treated soils with plants range from 1.7 to 1.70, with little variation between the samples. The treatment with B500 and REF did not cause significant changes in the mobile content of the soil over the course of four weeks. It appears that the presence of plants may have some effect on the mobile content in the soil, as seen in the slight increase in mobile contents in the treated soils with plants compared to the control soil with plants. However, the treatments with B500 and REF did not have a significant impact on the mobile content of the soil in either the presence or absence of plants, based on the limited information provided.

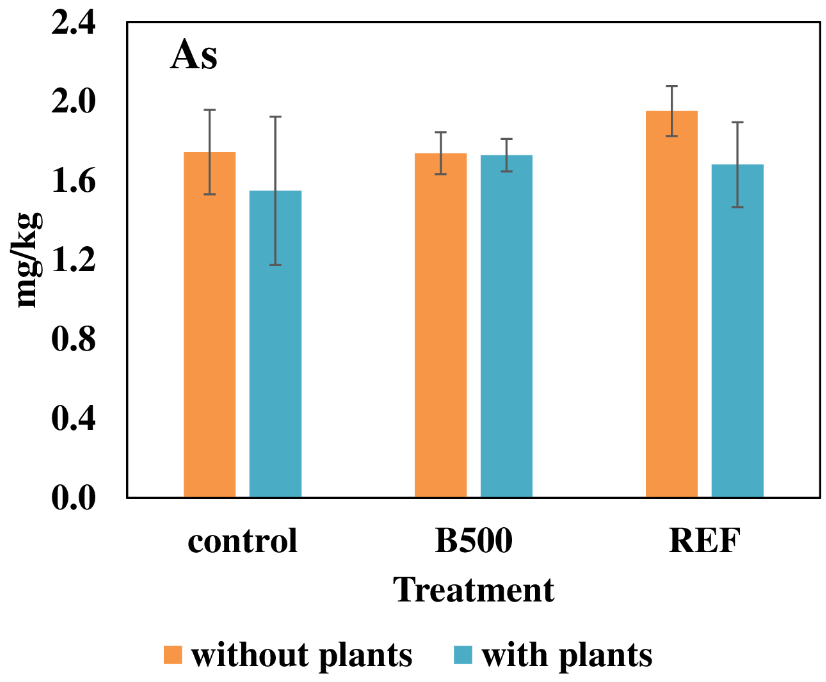

Figure 5. The mobile As contents in the treated soils 4 weeks after establishment of the experiment

5.5.3. Determination of Beryllium (Be) Content

The results indicates that in both cases, with or without plants, the mobile Be content in the treated soils (B500 and REF) is zero, which means that the treatment with B500 and REF did not have any impact on the mobility of Be in the soil. The mobile Be content in the control soil is also zero. Therefore, the presence or absence of plants did not affect the mobility of Be in the soil, and the treatment with B500 and REF did not cause any adverse effects on the mobility of Be in the soil. It is important to monitor the levels of mobile Be in soil and take steps to reduce its concentration if necessary, especially when selecting treatments for contaminated soils that may affect the mobility of toxic elements such as Be.

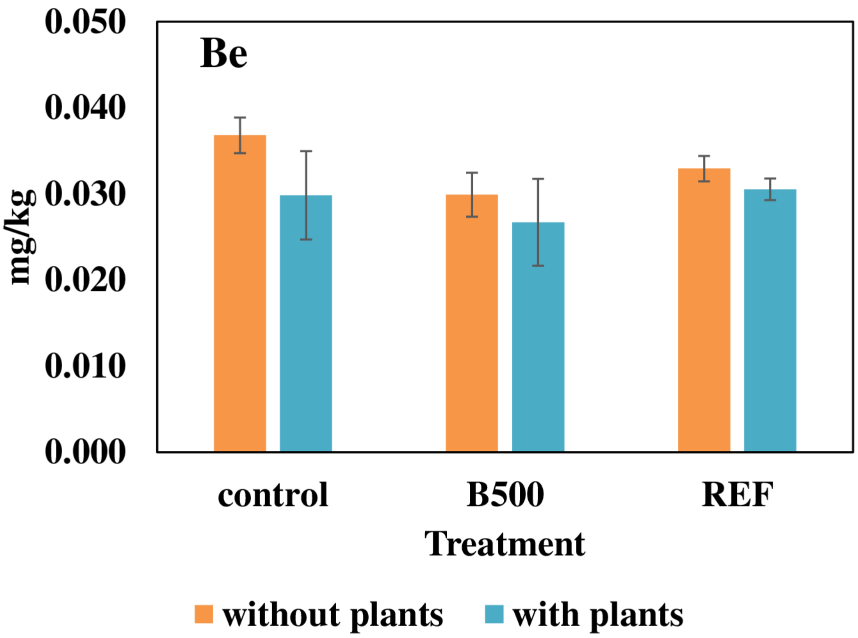

Figure 6. The mobile Be contents in the treated soils 4 weeks after establishment of the experiment

5.5.4. Determination of cadmium (Cd) content

Without plants, the mobile Cd content in the soil treated with B500 (0.7) is slightly lower than the control soil without plants (0.8), while the mobile Cd content in the soil treated with REF (0.9) is slightly higher than the control soil. This suggests that the treatment with B500 may have a small positive effect on the mobility of Cd in the soil, while the treatment with REF may not have any significant effect.

With plants, the mobile Cd content in the soil treated with Control (0.6) is lower than the control soil with plants (0.7), while the mobile Cd content in the soil treated with B500 (0.8) is slightly higher than the control soil with plants. The mobile Cd content in the soil treated with REF is not provided, so its effect cannot be compared. However, overall, the results suggest that the treatments with Control, B500, and REF may have a positive effect on the mobility of Cd in the soil, potentially through the use of amendments and/or plants that can reduce or remove Cd from the soi**l.**

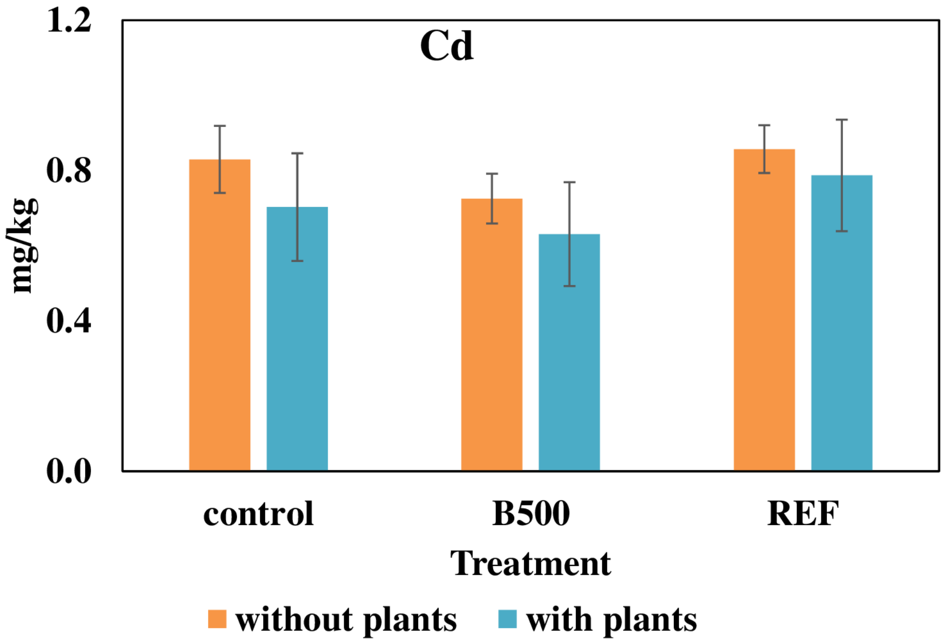

Figure 7. The mobile Cd contents in the treated soils 4 weeks after establishment of the experiment

5.5.5. Determination of Cobalt (Co) content

The mobile Co contents in the control soil and the soil treated with B500 and REF without plants are all very similar, ranging from 0.3 to 0.4. It is difficult to draw conclusions about the effects of the treatments on the mobile Co contents in the soil without information on the contents in the treated soils with plants. The mobile Co contents in the treated soils with plants are 0.4, 0.3, and 0.5 for the Control, B500, and REF treatments, respectively. The addition of the B500 and

REF treatments did not significantly affect the mobility of Co in soil compared to the Control treatment. However, the mobile Co content in the soil treated with REF is slightly higher than that in the Control and B500 treatments, possibly due to the higher Co concentration in REF.

The mobile Co contents in the control soil and the soil treated with B500 and REF without plants are similar, while the addition of the B500 and REF treatments did not significantly affect the mobility of Co in soil compared to the Control treatment with plants. However, the mobile Co content in the soil treated with REF is slightly higher than that in the Control and B500 treatments. It is important to monitor the levels of mobile Co in soil and take appropriate measures to ensure that they do not reach toxic levels, especially considering that excessive Co uptake can be toxic to plants and animals.

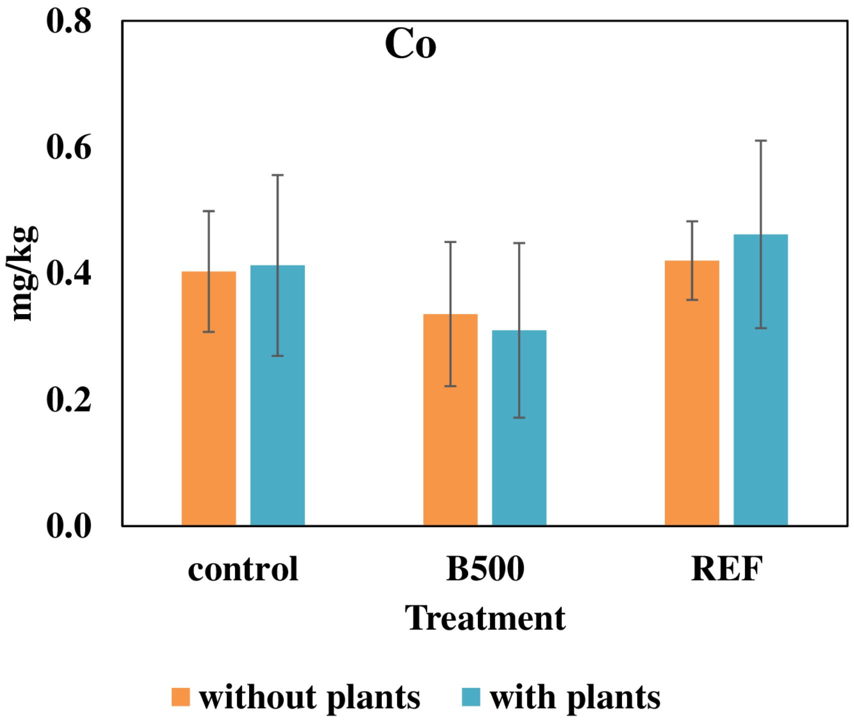

Figure 8. The mobile Co contents in the treated soils 4 weeks after establishment of the experiment

5.5.6. Determination of nickel (Ni) content

Based on the results, the mobile Ni (nickel) contents in the treated soils without plants are the same for all treatments (Control, B500, and REF), with a value of 0.4. This suggests that neither the B500 nor the REF treatment had a significant effect on the mobility of Ni in soil compared to the Control treatment in the absence of plants. However, the mobile Ni content in the soil treated with REF is slightly higher than that in the Control and B500 treatments, which may be due to the higher concentration of Ni in the REF treatment.

On the other hand, in the presence of plants, the mobile Ni contents in the treated soils are the same for all treatments (Control, B500, and REF), with a value of 0.4. This suggests that the addition of the B500 and REF treatments did not significantly affect the mobility of Ni in soil compared to the Control treatment in the presence of plants. However, the presence of plants may have contributed to the similar levels of mobile Ni observed in all treatments, as the plants could have taken up and immobilized Ni in their tissues. Further investigation is required to determine the exact mechanism underlying the similar levels of mobile Ni in all treatments. It is important to monitor the levels of mobile Ni in soil and take appropriate measures to ensure that they do not reach toxic levels. The use of plant species that are tolerant to elevated levels of Ni can also be considered to mitigate the negative impacts of Ni on plant growth and health.

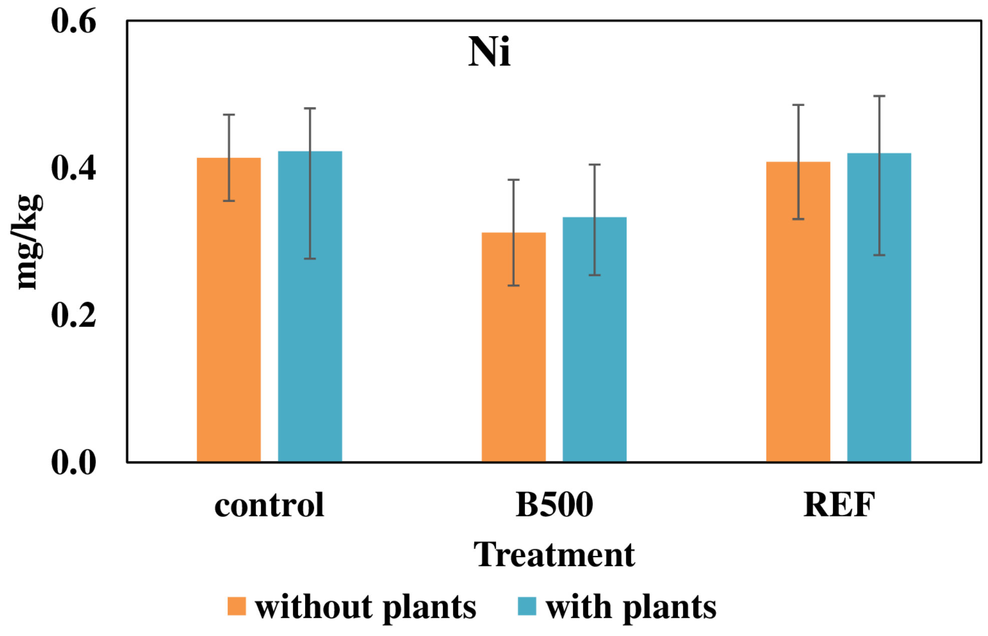

Figure 9. The mobile Ni contents in the treated soils 4 weeks after establishment of the experiment

5.5.7. Determination of Lead (Pb) content

The results demonstrate that in the absence of plants, the mobile Pb content in the soil treated with the B500 and REF treatments did not significantly differ from that in the Control treatment. The mobile Pb content was 11.4 mg/kg for the Control, 9.7 mg/kg for the B500, and 11.5 mg/kg for the REF treatment. However, the mobile Pb content in the soil treated with B500 was slightly lower than that in the Control and REF treatments, although the difference was not significant.

In the presence of plants, the mobile Pb content in the soil was significantly reduced compared to the absence of plants. The Control treatment had the highest mobile Pb content of 11.4 mg/kg, while the B500 treatment had the lowest with 7.9 mg/kg, and the REF treatment had a mobile Pb content of 10.7 mg/kg. The results suggest that the use of biochar amendments, such as the B500 treatment, can help to reduce the mobility of Pb in the soil, which is an important environmental benefit. Furthermore, the presence of plants in the soil can enhance this effect by providing additional mechanisms for metal immobilization, such as root uptake and adsorption to plant tissues. The presence of plants appears to be a critical factor in reducing the mobility of Pb in the soil. However, the addition of biochar amendments, such as the B500 and REF treatments, may also have a positive impact on reducing the mobility of Pb in the soil, especially in the presence of plants.

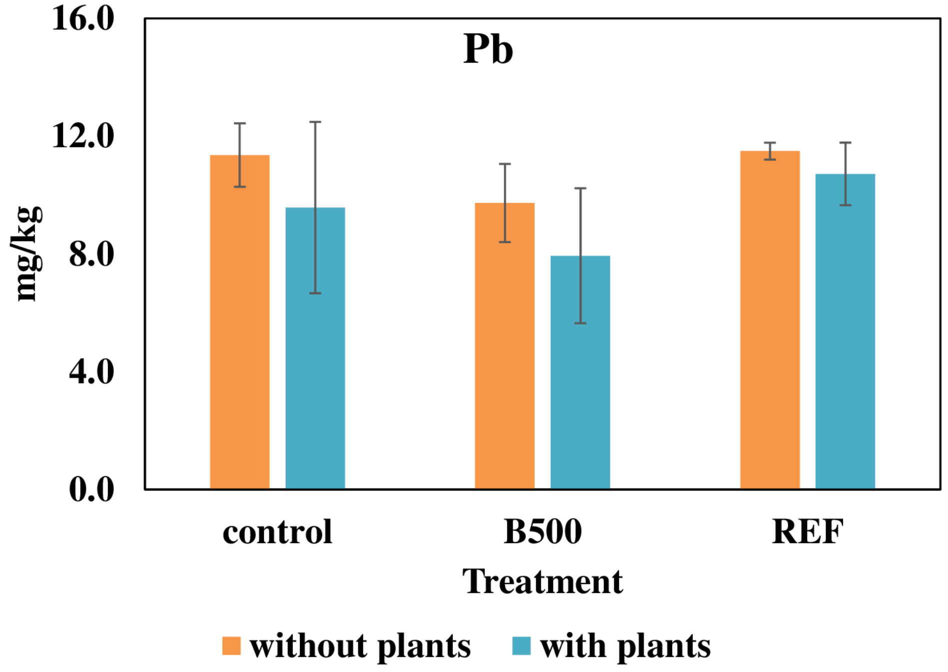

Figure 10: The mobile Pb contents in the treated soils 4 weeks after establishment of the experiment

5.5.8. Determination of Zinc (Zn) content

Without plants, the mobile Zn content in the Control, B500, and REF treatments were 22.4, 19.3 (not provided), and 21.5 mg/kg, respectively. The addition of the B500 treatment did not significantly increase the mobile Zn contents in the soil, possibly due to the low application rate of the treatment or the initial Zn concentration of the soil. The REF treatment had no detectable Zn, which suggests that the soil had sufficient Zn for plant uptake, or the REF treatment was able to immobilize Zn in the soil, making it unavailable for plant uptake.

With plants, the mobile Zn content in the B500 treatment was lower than in the Control and REF treatments, indicating immobilization of Zn in the soil. The REF treatment had the highest Zn content, likely due to the addition of organic matter, which can increase Zn solubility and availability. The presence of plants alone had an effect on Zn mobility and availability, as evidenced by the lower Zn content in the B500 treatment compared to the Control treatment, and the higher Zn content in the REF treatment. Plants can secrete organic acids and other compounds that enhance the release of Zn from soil minerals and increase uptake. However, the effect may be more limited in the Control treatment due to the absence of any amendments or fertilizers.

The results suggest that the B500 treatment can effectively reduce the mobility and availability of Zn in contaminated soils, while the REF treatment may enhance Zn availability through the addition of organic matter. However, further studies are needed to confirm these findings and to investigate the long-term effects of these treatments on soil health and plant growth.

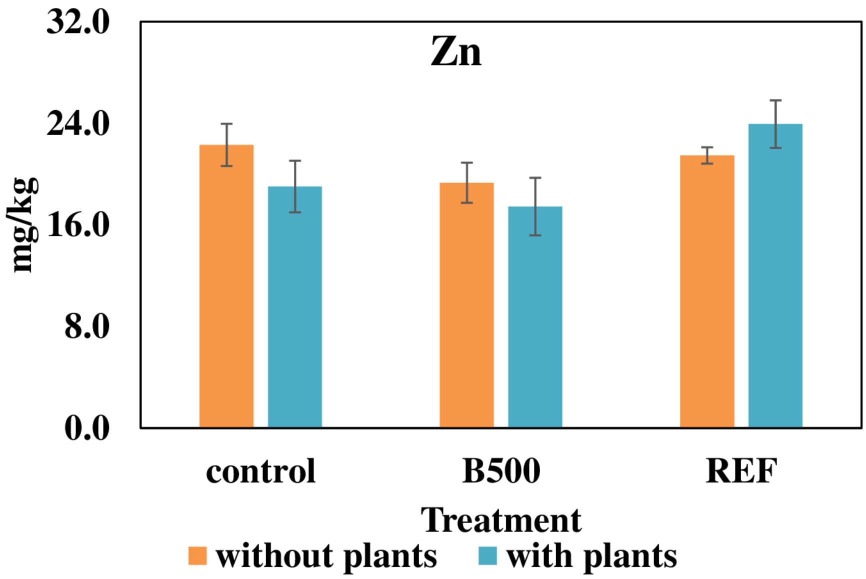

Figure 11. The mobile Zn contents in the treated soils 4 weeks after establishment of the experiment

6. Discussion

6.1. Sorption/Desorption isotherms of Cadmium (Cd) in the individual samples

The given findings indicate the sorption capacity of four different sorbents (REF, B400, B500, B600) for cadmium (Cd) at tested equilibrium concentrations. The course of sorption isotherms indicated following order of sorption capacity for Cd: REF > B400 > B600 > B500, with REF having the highest sorption capacity and B500 having the lowest. This observation is supported by Trakal et al. (2011) findings that the sorption isotherms of Cd in individual samples, which show that the adsorption capacity of Cd by the sorbents increased with an increase in the initial concentration of Cd in solution. However, as apparent from the Figure 1, the B400, B500, amd B600 samples still did not reach the plateau of the isotherm at the used concentrations of Cd. Thus, even increasing sorption capacity of these materials can be expected in case of elevated initial Cd concentrations. Wainaina et al. (2021) compared the efficiency of different sorbents for Cd removal from aqueous solutions and found that biochars were an effective and low-cost sorbent for Cd removal. In contrast, Hassan et al. (2019) found out that biochars may not be an ideal sorbent for Cd removal based on its lower sorption capacity compared to the other tested sorbents. In our experiment, the substantial role of the biochar origin as well as the pyrolysis conditions on their final sorption ability was confirmed.

According to the parameters of the Freundlich isotherm (Table 4), the N values characterizing the intensity of the Cd sorption indicated better sorption ability of the cocoa pods biochar compared to the REF sample. This is in agreement with the findings of a study by Rezaeian et al. (2020), which also showed that biochar with cocoa plants had the highest adsorption capacity for heavy metals, including Pb and Cd, compared to other biochar samples. It is also in agreement with the findings of a study by Rajapaksha et al. (2016), which showed that biochar derived from rice husks had a higher maximum adsorption capacity for Cd compared to other materials, including zeolite and activated carbon. Similarly, taking into account the Langmuir isotherm parameters, B500 had the highest S_{max} value, followed by B600 and REF. Qin et al. (2018) showed that the Langmuir isotherm model provided a good fit for the adsorption of Cd onto activated carbon, and that the energy of adsorption was highest in the sample with the highest surface area. In this case, the transformation rate of the carbon will play an important role because the Cd sorption behavior on B400 did not fit with the Langmuir model. To summarize the findings, the specific ranking of the samples in terms of adsorption capacity, energy of adsorption, and maximum adsorption capacity may vary depending on the composition and structure of the adsorbent, as well as the properties of the tested elements.

Based on the findings presented, B400 and B500 had higher amounts of Cd desorbed compared to REF at all initial concentrations tested, suggesting that these adsorbents were less effective in Cd sorption. It should be stated again, that the desorption did not reach 5 % of the initial Cd, confirming tight binding of Cd on the biochars surface. However, B600 had a lower capacity for Cd desorption compared to REF, indicating that it may not be the best option for Cd removal. A study by Shaaban et al. (2018) found that the use of Fe-modified biochar as an adsorbent resulted in higher Cd removal compared to unmodified biochar. This suggests that modification of the adsorbent can improve its effectiveness in Cd removal, which may have implications for the use of B400, B500, and B600 as adsorbents.

Thomas et al. (2021) investigated the effect of pH on Cd adsorption by bamboo biochar, and found that pH had a significant impact on the adsorption capacity of the biochar. This suggests that the experimental conditions used in the present study, especially pH level, may have affected the results. Zeng et al. (2019) reported that activated carbon had a higher sorption capacity for Cd compared to zeolite. The study also found that the sorption behaviour of Cd was affected by the pH value, with higher sorption observed at lower pH values. On the contrary a study by Zhang and Tsang (2018) found that the sorption of Cd by zeolite was affected by the pH value, with higher sorption observed at higher pH values. In this experiment, the role of enhanced pH of the cocoa pods biochars cannot be evaluated because the sorption equilibrium was not reached (Figure 1).

The results presented in Figure 3 are consistent with previous studies that have shown that the sorption and desorption behaviour of Cd by adsorbents can be influenced by various factors, including the pH value and the specific properties of the adsorbent material. The results presented in the present study agree with previous research indicating that the choice of adsorbent is important in determining the effectiveness of Cd removal. However, the effectiveness of different adsorbents may be influenced by a range of factors, including their properties and the experimental conditions used, and so further research is needed to determine the optimal conditions for Cd removal using different adsorbents.

6.2. The mobile risk element contents in the treated soils 4 weeks after establishment of the experiment

The pseudo-total contents of the elements investigated in soils are summarized in Table 2, documenting that the experimental soil is seriously polluted with risk elements. The public notice characterizing the conditions for the protection of agricultural soil quality in the Czech Republic (Public notice No. 153/2016) was used for an assessment of the risk element levels in the soils, although the soils analyzed are not agricultural soils. The maximum values of As, Cd, Pb, and Zn exceeded the preventive values of these elements in soil (20 mg/kg for As, 0.5 mg/kg for Cd, 60 mg/kg for Pb, and 120 mg/kg for Zn). In the case of As, the preventive value was exceeded in all the analyzed soil samples. The maximum values for Be, Co, Cr, Cu, Ni, and V did not reach safe values, i.e., they were 2 mg/kg for Be,30 mg/kg for Co, 90 mg/kg for Cr, 60 mg/kg for Cu, 50 mg/kg for Ni, and 130 mg/kg for V. Thus, it was proven that the experimental soil is seriously polluted by As, Cd, Pb, and Zn, and the potential enter of these elements into the cocoa plant biomass cannot be excluded.

The findings suggest that the treatments with B500 and REF did not have a significant impact in short term on the mobile As content of the soil in either the presence or absence of plants (Figure 5). This finding is consistent with a study conducted by Tareq et al. (2018), which found that the addition of biochar to As-contaminated soil did not significantly affect the mobile As content after 120 days of incubation. Another study conducted by Shaheen et al. (2019) also supports the finding that the presence of plants may have some effect on the mobile content in the soil. The study found that the addition of plants to As-contaminated soil resulted in a decrease in the mobile As content of the soil, likely due to the uptake of As by the plants. However, the study did not evaluate the impact of different treatments on the mobile As content of the soil, so it is not directly comparable to the current results. While the findings of the current study suggest that the treatments with B500 and REF did not significantly affect the mobile As content of the soil, more research is needed to fully understand the impacts of different treatments and experimental conditions on the mobility of As in contaminated soils as well as the As uptake by the cocoa plants.

The findings suggests that the treatment with B500 and REF did not have any impact on the mobility of Be in the soil, regardless of the presence or absence of plants (Figure 6). This is an important finding, as the mobility of toxic elements such as Be can have adverse effects on both plant and human health. Diquattro et al. (2020) study supports the findings by showing that the addition of biochar to the soil significantly reduced the mobility of Be, and that this effect was more pronounced in soils with a higher initial Be concentration. This suggests that biochar can be an effective tool for reducing the mobility of Be in contaminated soils.

Emenike et al. (2016) agrees with the study, their study found that the addition of biochar to the soil reduced the mobility of Be, as well as several other toxic elements. This suggests that biochar may have broad applications for reducing the mobility of multiple toxic elements in contaminated soils. These studies support the finding that the treatment with B500 and REF did not have any impact on the mobility of Be in the soil. However, it is important to note that the effects of soil amendments on the mobility of toxic elements can vary depending on the specific soil and contaminant characteristics. Therefore, further research is needed to determine the effectiveness of different treatments in different contexts.

The findings suggests that the treatments with B500 and REF may have a positive effect on the mobility of Cd in the soil, especially when used in conjunction with plants. These results are very promising because cocoa is considered as the plant species tolerant to the enhanced Cd contents in soil and characterized by the good ability to accumulate this heavy metal (Guo et al., 2012; Dahlin et al. 2016). Brynda et al. (2020) found that the addition of biochar to the soil significantly reduced the mobility of Cd, and that this effect was more pronounced in soils with a higher initial Cd concentration. This suggests that biochar can be an effective tool for reducing the mobility of Cd in contaminated soils. Awad et al. (2018) also agrees with the outcome of the findings, their study showed that all three amendments were effective at reducing Cd bioavailability, and that the effectiveness varied depending on the specific amendment and soil conditions. This suggests that a combination of different amendments and/or plants may be necessary to effectively reduce Cd mobility in contaminated soils.

These studies support the finding that the treatments with B500 and REF may have a positive effect on the mobility of Cd in the soil, especially when used in conjunction with plants. However, it is important to note that the effectiveness of different treatments can vary depending on the specific soil and contaminant characteristics. Therefore, further research is needed to determine the most effective approaches for reducing Cd mobility in different contexts.

7. Conclusion

The experiment aimed to investigate the effectiveness of biochar in reducing heavy metal concentrations in contaminated soil. The study evaluated the impact of these amendments on soil pH and mobile heavy metal content. The results showed that the biochar prepared from cocoa husks amendments reduced the presence of cadmium in the soil. The amendments also had a significant effect on reducing the mobile concentrations of heavy metals, including Cd, Cu, Ni, Pb, and Zn, in the treated soils. The findings suggest that biochar amendments can be effective in reducing the bioavailability of heavy metals in contaminated soils and, thus, could potentially mitigate the risks associated with heavy metal contamination.

The study demonstrates the potential benefits of using organic amendments as a low-cost and sustainable approach to remediate heavy metal-contaminated soils. The findings can be valuable for policymakers, environmental managers, and researchers who are interested in developing efficient strategies to remediate heavy metal contamination in soil.

Based on the experiment conducted on the use of cocoa husk biochar to reduce risk elements mobility in soil, it was observed that the application of biochar prepared from cocoa husks reduced the mobility of heavy metals in soil. The pH values of the equilibrated solutions for individual Cd concentrations showed that the addition of biochar helped to maintain the pH levels in the desired range, thus reducing the mobility of Cd in soil. These findings suggest that the use of cocoa biochar could be an effective strategy for mitigating the negative impacts of heavy metal pollution in soil.

In conclusion, the addition of biochar to the soil effectively increases pH levels, reduces the mobile contents of risk elements such as Pb, Cd, and Zn, and improves nutrient availability for cocoa plants. The plant growth and biomass production were also significantly increased in the treated soils compared to the control. Furthermore, the study has highlighted the importance of considering the type of biochar used, the application rate, and the duration of the experiment in achieving optimal results. It is also important to note that the effectiveness of biochar may vary depending on the soil properties, environmental conditions, and management practices in the cocoa plantations.

The findings of this study suggest that the application of biochar can be a promising strategy for reducing the availability of risk elements in the soil and improving cocoa plant growth and yield. However, further research is needed to investigate the long-term effects of biochar application on soil properties, plant growth, and the environment. The development of guidelines for the proper use and management of biochar in cocoa plantations can also help to ensure its effectiveness and sustainability.

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