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## The influence of various organic amendments on the bioavailability and plant uptake of cadmium present in mine-degraded soil



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#### HIGHLIGHTS

#### GRAPHICAL ABSTRACT

- Biochar, bagasse, rice husk and maizecomb were applied at 3 and 5% to Cdsoil.
- Biochar as geosorbent was the most effective at reducing Cd bioavailability.
- Biochar significantly  $(P < 0.01)$  increased chlorophyll/biomass of tomato and cucumber.
- Biochar significantly decreased Cduptake in tomato (24–30%) and cucumber (36–54%).
- Biochar addition significantly reduced health risk via ingestion of selected plants.

### article info abstract

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#### Mining of minerals and precious elements leads to land degradation that need to be reclaimed using environmentally friendly and cost effective techniques. The present study investigated the potential effects of different organic amendments on cadmium (Cd) bioavailability in mining-degraded soil and its subsequent bioaccumulation in tomato and cucumber. The selected organic geosorbents (hard wood biochar (HWB), bagasse (BG), rice husk (RH), and maize comb waste (MCW)) were added at application rates of 3% and 5% to chromite minedegraded soil containing Cd. Tomato and cucumber plants were then grown in the soil, and the roots, shoots, leaves, and fruits of each plant were analysed for Cd concentration, biomass production, and chlorophyll content. The results indicated that the different organic materials have variable effects on physiochemical characteristics of vegetables and Cd bioavailability. The biochar amendment significantly  $(P < 0.01)$  increased chlorophyll contents (20–40%) and biomass (40–63%), as did RH to a lesser extent (increase of 10–18% in chlorophyll content and 3–45% in biomass). Among the amendments, HWB was the most effective at reducing Cd bioavailability, wherein significant decreases were observed in Cd uptake by fruits of tomato (24–30%) and cucumber (36–54%). The higher application rate of 5% was found to be more effective for mitigation of Cd mobility and bioaccumulation in plants grown in mine degraded soil. The study results indicate that effective use of organic amendments, especially HWB, can significantly reduce Cd levels in vegetables, improve food quality, and reduce human-health risk while increasing biomass production.

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The contamination of agricultural soils with cadmium (Cd) has steadily increased during the last few decades due to multiple factors. Firstly, intensive mining, pesticides, chemical fertilizers, and smelting discharge Cd to the environment. Secondly, Cd is widely used in pigments, nickel-Cd batteries, alloys, stabilizers, electronics, electroplating, power generation and vehicle industries [\(WHO, 2011\)](#page--1-0). Mine degraded soils are generally poorly structured with no or very scarce vegetation due to the presence of high concentrations of toxic metals, particularly Cd [\(Nawab et al., 2015](#page--1-0)). Mining activities release a large amount of Cd ranging from 2 to 16.5 mg  $kg^{-1}$  ([Khan et al., 2017, 2018](#page--1-0)). Plants grown on mine impacted soil have the potential to accumulate high concentration of Cd ([Zhao et al., 2014\)](#page--1-0). Disposal of waste materials during manufacturing and use of these products and processes results in pathways for Cd entry into the environment, for example land application of biosolids and irrigation with wastewater ([Khan et al., 2014;](#page--1-0) [Zhang et al., 2010\)](#page--1-0). Cd is a non-essential and potentially toxic element to all organisms [\(Benavides et al., 2005\)](#page--1-0). For example, high Cd exposure causes bone and kidney damage, cancer, and haematuria ([Han et al.,](#page--1-0) [2013](#page--1-0); [Satarug et al., 2010\)](#page--1-0). Due to its wide range of sources and ubiquitous occurrence, Cd has become an important environmental pollutant.

The uptake of Cd by vegetables from contaminated soil is a primary starting point of exposure for humans ([Khan et al., 2015\)](#page--1-0). The uptake of Cd from soil by roots, and its subsequent translocation in plants is a very complex process. The mobility of Cd in soil and its uptake by plants depend on several factors including its concentration in soil, type of plant, pH, soil organic matter, cation exchange capacity (CEC), and concentrations of iron and zinc [\(Meeus et al., 2002\)](#page--1-0). The bioaccumulation capacity of Cd is different for different plants. The leafy vegetables accumulate the highest concentration of Cd followed by root vegetables and grains [\(Khan et al., 2017](#page--1-0)). High concentrations of Cd in soils pose great risk of dietary intake due to its high toxicity and enhanced uptake by plants [\(Liu et al., 2003](#page--1-0)).

Cd uptake by plants and resultant dietary exposure can be alleviated by reducing Cd concentrations in soil or by reducing its bioavailability to food plants [\(Bashir et al., 2018](#page--1-0); [Kumpiene et al., 2008;](#page--1-0) [Mulligan et al.,](#page--1-0) [2001](#page--1-0)). Soil remediation by reducing heavy metals mobility and bioavailability is an efficient and cost effective method to address the issue of metals toxicity ([Bashir et al., 2018](#page--1-0); [Li et al., 2018\)](#page--1-0). Methods for reducing soil concentrations include phytoremediation, soil washing, electrokinetic remediation, and excavation, while methods for reducing bioavailability include stabilization and solidification [\(Khan et al., 2017, 2018](#page--1-0)). One of the latter techniques is the in situ stabilization of metals by the addition of materials that exhibit high metal retention capacity. Different types of organic materials such as compost from the food industry, municipal waste solids, and manures and agriculture residues may be used for the remediation of metals contaminated soils ([Qi et al., 2018](#page--1-0)). It is reported that organic materials have the ability to decrease metals availability by increasing the soil pH and by complexation via the reactive groups present in organic materials ([Abbas et al., 2017;](#page--1-0) [Karlsson](#page--1-0) [et al., 2007](#page--1-0)). Similarly, some studies revealed that the increase in soil pH with application of biochar may affect the nutrient availabilities and plant uptakes ([Qi et al., 2017](#page--1-0)).

Biochar derived from industrial, municipal, agriculture and food wastes can also be very beneficial for the remediation of metalscontaminated soils [\(Khan et al., 2015;](#page--1-0) [Khan et al., 2018;](#page--1-0) [Li et al., 2018;](#page--1-0) [Ahmad et al., 2014;](#page--1-0) [Cao and Harris, 2010](#page--1-0)). The application of biochar to soil increases the water holding capacity, enhances the calcium (Ca), phosphorous (P), and nitrogen (N) status ([Borchard et al., 2012;](#page--1-0) [Lehmann, 2007\)](#page--1-0), and the bioavailability of Mg, Zn, and Ca ([Gartler](#page--1-0) [et al., 2013](#page--1-0); [Major et al., 2010\)](#page--1-0).

Previously, several studies have been conducted to assess the role of biochar and organic materials in remediation of metal degraded soil. However, to authors information no such comprehensive study has been conducted to evaluate the effects of organic amendments

including non-biochar materials i.e. bagasse (BG), rice husk (RH), and maize comb waste (MCW), and hard-wood derived biochar (HWB) on uptake of Cd, vegetable growth, biomass production, and chlorophyll content. The present study was conducted to investigate their potential use and compare the efficiency of these amendments for the reclamation of mining degraded soils and Cd availability to vegetables. Greenhouse experiments were conducted to compare the effects of four selected amendments on the availability, uptake, and translocation of Cd by tomato and cucumber grown in different geosorbent-amended mine degraded soils.

#### 2. Materials and methods

### 2.1. Soil and amendment characteristics

Soil samples were collected from the 0–20 cm interval of agricultural fields at multiple mine-impacted sites in the Heroshah area of Malakand Agency, Pakistan. Each sample was thoroughly mixed in the laboratory to obtain a homogenized sample, and then air dried and passed through a 2-mm mesh. The soil was analysed for total Cd concentration using standard methods [\(Nezhad et al., 2014](#page--1-0)). Briefly, 0.5 g sample was digested with aqua regia using an automatic controlled digestion block. After completion of digestion, the extracts were cooled to room temperature and then filtered into 50-ml corning tubes and diluted with deionized water and the metal concentrations were determined using ICP-OES (Perkin-Elmer OPTIMA-2000, USA). The concentrations of P and potassium (K) were determined using UV-spectrophotometer and flame photometer, respectively. The total N concentration was measured using the Kjeldahl method [\(Khan et al., 2016](#page--1-0)).

Organic materials including bagasse (BG), rice husk (RH), maize comb waste (MCW), and hard-wood derived biochar (HWB) were selected as amendment materials. The organic amendments used in the experiments were ground and passed through a 2-mm mesh before application to the soil. HWB was prepared through pyrolysis technique at 500 °C in the absence of oxygen [\(Khan et al., 2013](#page--1-0)).

#### 2.2. Greenhouse experiments

The four amendments were applied to the soil at  $3\%$  and  $5\%$  (w/w) application rates (afterward referred as BG3, BG5, RH3, RH5, MCW3, MCW5, HWB3 and HWB5) and thoroughly mixed. Plastic pots were filled with 4 kg of the soil (dry weight, d.w). NPK doses were applied at concentrations of 60, 35, and 40 mg  $kg^{-1}$  using NH<sub>4</sub>NO<sub>3</sub>, and K2HPO4 fertilizers, respectively. Each amendment and control (without amendment) were prepared in triplicate. Two sets (one for tomato and second for cucumber) of the selected treatments were prepared. All pots were evenly irrigated with deionized water when needed. The positions of the pots were changed from time to time to ensure the availability of equal amount of light to each pot.

Seeds of tomato (Cherry tomato (Lycopersicon esculentum)) and cucumber (Cucumis sativus) were obtained from Tarnab botanical garden, Peshawar. The seeds of tomato were washed using  $H_2O_2$  first and then with deionized water. After washing, the seeds were germinated in petri dishes. The seedlings were provided a controlled environment of 23  $\pm$  2 °C and 12/12 photoperiod (light/dark). After germination, healthy and uniform seedlings were transferred in equal number to each pot. Cucumber seeds were directly germinated in the selected pots. The pots were kept in the greenhouse under controlled environment. The physiological characteristics and leaf chlorophyll content were measured periodically at different stages of plant growth. The chlorophyll content was measured using a soil-plant analysis development (SPAD) chlorophyll meter (atLEAF, PN: 0131, USA) [\(Ling et al.,](#page--1-0) [2011](#page--1-0)). For the measurement of chlorophyll content, five leaves in each pot were randomly selected and SPAD readings were recorded in triplicates

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