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Biochar and Phosphorus-Loaded Biochar Derived from Wood Chips or Poultry Manure Reduced Availability and Uptake of Cadmium by Plants from Cd-Contamanated Soils

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ABSTRACT

This study investigated the effect of biochar (BC) and phosphorous-loaded biochar (P-BC) derived from wood chips and poultry manure on soil cadmium availability to plants in Cd-contaminated soils. The wood chips (WC) and poultry manure (PM) pyrolyzed at 400 °C to produce BCs samples. Additionally, BC samples were treated with KH_2PO_4 solution to produce P-BC. The effectiveness of produced BCs in removing Cd ions from aqueous solutions containing 1, 10, 25, 50, and 100 mg Cd L^{-1} was examined and the Cd^{2+} adsorption was described using Freundlich, Langmuir, and Temkin isotherm models. A pot experiment was also carried out to assess WC-BC, WCP-BC, PM-BC, and PMP-BC impacts on the growth, nutrients uptake, and availability of P and cadmium to wheat plants in soils spiked with 1, 10, 100, and 1000 mg Cd kg^{-1} soil. The BCs were applied to soil at a level of 3% (w:w). The results of the adsorption experiment showed that Freundlich model fitted the Cd adsorption (R^2= 0.9962 – 0.9988) more than other isotherm models. The P-BCs application increased soil available P, plant growth and N, P, K uptakes. Meanwhile the soil available Cd, shoot Cd concentrations and its uptake decreased compared to BCs and control. The PM-BC was better than the WC-derived ones in improving these parameters. Applying BC and P-BC to Cd-contaminated soil introduce a promising tool to immobilize cadmium with positive impacts on soil properties and plant growth. Additionally, these biochars can be used for Cd^{2+} removing from aqueous solutions and waste-polluted water.

Keywords: Soil contamination; Biochar; Cadmium; Soil remediation.

INTRODUCTION

Degradation of the environment is one of the main problems that society is currently experiencing. Numerous data show a dramatic rise in the depletion of water resources and soils that are important for agriculture (Naorem *et al*., 2023). Heavy metal (HM) contamination of agricultural soils is one of the major environmental issues that threatens human health and the security of agricultural produce (Adnan *et al*., 2024). Anthropogenic activities like mining and industrialization, as well as widespread use of agrochemicals like pesticides, fertilizers, and sewage irrigation, are the main causes of heavy metal pollution in water, wastewater, and soils (Shakti & Pandey, 2024). Heavy metals like nickel (Ni), lead (Pb), mercury (Hg), cadmium (Cd), and chromium (Cr) have been more prevalent in soil over the past decade (Angon *et al*., 2024). Moreover, these metals are regarded as permanent and persistent pollutants when they are released into the environment since they cannot be degraded by chemicals processes or microorganisms (Mishra *et al*., 2019). Heavy metals have harmful impacts on plants, animals, soil microbial activity, and soil fertility and they can accumulate throughout the food chain, causing toxic effects for human (Tauqeer *et al*., 2022). The well-known toxic heavy metal cadmium (Cd^{2+}) is a major pollutant that can be hazardous to the environment and public health due to its high mobility, potential toxicity, and lack of biodegradability (Irshad *et al*., 2023). Significant harm to the kidneys, bones, skin, brain, pancreas, liver, myocardium, immune system, and the central nervous system can result from cadmium exposure (Leal *et al*., 2023). In agricultural soils, cadmium pollution results from a mix of natural geological formations and human activity such mining, fertilizer use, and atmospheric deposition. Additionally, Cd using in various industrial processes results in aqueous solutions with elevated concentrations that can contaminate soil and water. In addition to degrading soil, cadmium pollution can harm plant growth and metabolism. One remediation approach that has been developed is in-situ immobilization using chemical stabilization. The utilization of inexpensive adsorbents, such as waste products, agricultural byproducts, and biosorbents, for the rehabilitation of heavy metal-contaminated soil is receiving increased attention these days. According to recent studies, biochar can be utilized as green sorbents to remediate a variety of contaminated environmental components, including soil, water, and air (Al Masud *et al*., 2023). Biochar is a carbonaceous and porous material produced by pyrolyzing organic waste, such as wood, sewage sludge, animal waste, and crop residue, in an oxygen-starved environment (Khan *et al*., 2023). Biochar predominantly comprises mineral ash residues, moderately labile aliphatic carbon, and stable aromatic carbon. A small portion of biochar's carbon is labile and can be degraded by microorganisms over time. This degradation process

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contributes to the release of nutrients into the soil, which can enhance microbial activity. Almost C in biochar is stable resistant to chemical, thermal, and microbial decomposition. This stable fraction of biochar acts as a long-term carbon sink for extended periods—reach hundred years—thereby contributing to soil C sequestration (Lehmann *et al*., 2021). Due to its recalcitrant nature, biochar lasts longer in soil than traditional organic matter forms, offering a sustainable method of soil remediation (Joseph *et al*., 2021). As a result, biochar has attracted the interest of the world for its potential uses in agriculture and the environment. When applied to soil, biochar can enhance its physical characteristics by decreasing bulk density and increasing aeration, porosity, and water retention (Yadav *et al*., 2023). Because of its high cation exchange capacity, biochar preserves nutrients including potassium, phosphorus, and nitrogen in relation to soil fertility. It can act as a source of nutrients itself, especially if it produced from nutrient-rich feedstocks such as manure. it can release soluble nutrients which are important for plant growth (Zafar *et al*., 2023).

Biochar is considered an environmentally acceptable alternative to other remediation approaches because of its unique properties like rich surface functional groups, large surface area, high porosity, and cation exchange capacity, which allow it to be employed for the removal of a wide range of inorganic and organic pollutants (Gusiatin & Rouhani, 2023). Biochar is used to remediate heavy metals through different ways such as chemical and physical sorption, complexation, precipitation, and ion exchange (Usman *et al*., 2016; Yang *et al*., 2021). Furthermore, if appropriate modification is carried out, the surface of biochar can be further utilized to provide additional adsorption sites (Mo *et al*., 2024). Biochar can be modified in two ways: either by adding metallic compounds to the surface of the material to increase the number of active sites, or by chemically treating the material to add more functional groups (Qiu *et al*., 2022). Phosphate (P) received the most attention among modifying chemical agents due to its effectiveness, environmental friendliness, low corrosion, and less adverse effects (Zhang *et al*., 2020). Besides, phosphate-modified biochar might act as a as a slow-release phosphorus fertilizer to increase soil fertility (Yang *et al*., 2021). Prior research has indicated that one efficient method for immobilizing heavy metals is the precipitation of metal phosphate. Gao *et al*. (2020) found that after 90 days of incubation with a 3% level of phosphorus-containing biochar, the concentration of recovered HMs from soil could be reduced by at least 5.9%. Yu *et al*. (2024) demonstrated that the addition of mono potassium phosphate, di-potassium hydrogen phosphate, and tri-potassium phosphate-modified wheat straw biochar reduced the extracted Cd from the studied contaminated soil by 67.93%, 18.41%, and 31.30%, respectively over control. Daffalla (2023) found that the phosphoric acid-treated biochar exhibited a strong sorption capacity (99%) towards Cr (VI). According to Dechapanya & Khamwichit (2023), the chemical modification of biochar by phosphoric acid improved the Pb^{+2} removal from aqueous solutions. Also, Yang *et al*. (2021), biochar and P-modified biochar reduced the amount of DTPA-extractable Cr, Cu, Pb, and Zn, transformed them into more stable states, and decreased their ecological issues. Ahmad *et al*. (2018), showed that P-loaded biochar improved maize growth and reduced the amount of soil-labile heavy metals in a polluted mining area. Our hypothesis is that wood residues and poultry manure-biochar either in raw or phosphorus-modified form can be used for remediation of Cd-contaminated soil and water. Therefore, Cd-contaminated soils were treated with the prepared BCs to investigate their effects on: (1) Cadmium immobilization in the Cd-contaminated soil, (2) growth and Cd uptake potential of wheat plants, and (3) Soil P availability and NPK uptakes by wheat plants, (4) some soil chemical properties. Another aim is to evaluate the Cd^{+2} removal efficiency from aqueous solutions as well as to identify the adsorption isotherms of Cd on the different prepared types of biochar.

MATERIALS AND METHODS

Production of biochar / P-treated biochar amendments and their characterization

Feedstock's, wood chips and poultry manure were chosen for biochar (BC) production. Wood chips were obtained from a nearby carpenter shop, While the poultry manure was brought from a local poultry farm at Sohag City, Egypt. These wastes were first oven-dried for 2 h at 60 °C, compressed in an aluminum container with a fitted cap, closed tightly, and then pyrolyzed in a muffle furnace at 400 °C for 4 h under oxygen-limited conditions. After that, containers were taken out of the furnace and left to cool at room temperature and the produced BCs named as WC-BC (Wood chips biochar) and PM-BC (poultry manure biochar).

For producing phosphate-treated biochars, a solution containing 500 mg P L^{-1} was prepared in deionized water using potassium dihydrogen phosphate (KH_2PO_4) (Sigma-Aldrich). Each biochar of the previously prepared biochars (WC-BC and PM-BC) was immersed in P solution at a ratio of 1:1 (W:V) in a glass beaker and stirred well, left to air dry at room temperature for a week while stirring the mixture continuously. Then the phosphate-modified biochars were dried at a temperature of 40°C for 5 hours in a drying oven and grounded again to obtain biochar in a powder form. The produced P-modified biochars were named WCP-BC (P-modified wood chips biochar) and PMP-BC (P-modified poultry manure biochar).

A 1:20 (biochar: distilled water) suspension was prepared for measuring biochar pH by using pH meter (pH 211 microprocessor, HANNA Instruments, UK) and a glass electrode. The electrical conductivity (EC) of biochars was determined using the EC meter (Orion 150, USA) in the 1:20 biochar to water extract. The total C in biochars determined using the total carbon analyzer (ThermoFisher scientific). The prepared biochars were digested with sulfuric and hydrogen peroxide according to Enders & Lehmann (2012). Total N and P of biochars was determined in the digested samples using microkjeldahl procedure and spectrophotometer (Jackson, 1973). Available P in biochars was extracted using $NaHCO_3$ extraction method (Olsen *et al*., 1954). The P was analyzed by a molybdate-ascorbic acid method using UV/VIS spectrophotometer (Peak Instruments E-2100UV Spectrophotometer, USA) (Jackson, 1973), the absorbance was measured at 880 nm. The specific surface area (SSA) was determined from N_2 gas adsorption-desorption isotherms using BELSORP max II equipment, Japan. The samples were first outgassed under vacuum for 4 hours at 150 °C. The Brunauer-Emmett-Teller (BET) equation was used to calculate the BET surface area (S_{BET}) (Brunauer *et al*. 1938).

Moreover, the total pore volume was obtained using a single point method at p/po = 0.993, and the average pore size was estimated using Barret-Joyner-Halenda (BJH) method. The biochar characteristics were shown in Table 1.

Table 1. Characteristics of the studied biochar types.

Property	Unit	Biochar			
		WC	WCP	PM	PMP
pH (1: 20)	-	7.90	7.65	9.41	9.25
EC (1: 20)	dS m^{-1}	0.614	0.784	4.23	4.42
Total P	mg Kg^{-1}	233.52	759.08	25027.79	25793.94
Available P		43.49	375.68	1385.82	1647.29
Available K		906	1589	1163.33	1795
Total N	%	0.88	0.63	3.78	3.40
Total C	%	91.12	90.48	68.74	66.93
Surface area (S_{BET})	m^2 g^{-1}	4.633	4.290	6.072	5.932
Total pore volume	cm^3 g^{-1}	0.07033	0.06697	0.08041	0.07921
Average Pore size	Å	30.3611	25.959	26.4838	25.2838

Cadmium adsorption

The efficiency of the prepared pristine and P-treated biochars to adsorb Cd^{2+} from aqueous solutions or contaminated water was investigated via duplicate batch adsorption experiments. A fixed dose (0.1 g) of BCs and P-modified BCs were shaken at 150 rpm for 20 h at room temperature with 50 ml of cadmium nitrate ($Cd(NO_3)_2{\cdot}4H_2O$) (Alpha Chemika, India) solutions containing different Cd^{2+}concentrations of 1, 10, 25, 50 and 100 mg Cd L^{-1}. After equilibrium, the solutions were filtered with Whatman-42 filter papers and the atomic absorption spectrophotometer (Perkin Elmer, A. Analyst 400, USA) was used to determine the final aqueous phase concentration of Cd^{2+} in the filtered solutions. The adsorbed Cd^{2+} on the biochar (mg g^{-1}) calculated by following equation (1):

$$C_s = (C_o - C_e)\, V / M \qquad (1)$$

The following equation 2 was used to get the adsorbed cadmium percentage (%R):

$$\%R = (C_o - C_e)\, 100 / C_o \qquad (2)$$

Where C_s (mg g^{-1}) is the Cd^{2+} sorption capacity, C_e (mg L^{-1}) and C_o (mg L^{-1}) indicate the equilibrium and initial concentrations of Cd, respectively. V (L) is the solution volume, and M (g) is the biochar mass on the dry basis.

The experimental sorption data are described by equations involving equilibrium isotherms. In addition to offering some insight into the sorption mechanisms, the equation parameters and underlying thermodynamic assumptions of these equilibrium models also frequently reveal information on the surface characteristics and affinities of the sorbent. The adsorption data was fitted using the Langmuir, Freundlich, and Temkin isotherm equations. The linear forms of the Langmuir,Freundlich and Temkin models were described in the following equations 3, 4, and 5, respectively:

$$C_e/C_s = C_e/Q + 1/(bQ) \qquad (3)$$

$$\text{Log } C_s = (1/n) \text{ Log } C_e + \text{Log } K_F \qquad (4)$$

$$C_s = B_T \ln C_e + B_T \ln K_T \qquad (5)$$

Where: C_e (mmol L^{-1}) is the equilibrium solution phase concentration, C_s (mmol Kg^{-1}) is the equilibrium solid phase concentration, Q (mmol kg^{-1}) is the theoretical maximum sorption capacity of Langmuir isotherm, b (L $mmol^{-1}$) is the enthalpy related sorption constant which refers to the adsorption energy coefficient or the affinity index, n is the sorption intensity constant of Freundlich model, K_F (L kg^{-1}) is the sorption capacity constant. $B_T = RT/b$, *T* is the absolute temperature in Kelvin, *R* the universal gas constant (8.314 J/mol K^{-1}), *b* = Temkin isotherm constant, B_T (J mol^{-1}) and K_T L $mmol^{-1}$) are the heat of adsorption and the equilibrium binding constants, respectively.

To assess the sorption capabilities of various biochars, the distribution coefficient (K_d) was computed as follows:

$$K_d = C_s / C_e \qquad (7)$$

K_d (L g^{-1}) is defined as the ratio of the Cd^{2+} concentration in the solid phase (C_s) to that in the equilibrium solution (C_e) (Usman *et al.*, 2016).

Greenhouse pot experiment

Soil sample was taken from the Experimental Farm of the Faculty of Agriculture, Sohag University, El-kawamel city, Sohag, Egypt. The collected soil was air-dried, grinded, and passed through a 2-millimeter sieve. The sieved soil was analyzed for some physical and chemical properties. The soil particle-size distribution was determined using the pipette method according to Rowell (1994). Soil pH was measured in a 1:1 (soil: water) suspension by using pH meter and a glass electrode (McLean, 1982). The EC meter was used to measure the electrical conductivity (EC) of soil in a 1:1 soil to water extract (Jackson, 1973). The total calcium carbonate content (% $CaCO_3$) in soil was estimated by using the calcimeter method (Nelson, 1982). The wet oxidation of Walkley and Black procedure was used for soil organic matter (OM) % determination according to Jackson (1973). The soil cation exchange capacity (CEC) was determined using sodium acetate (1 M, pH = 8.2) for saturation and ammonium acetate (1 M, pH = 7) for replacement (Baruah & Barthakur, 1997). Total nitrogen (%) in soil was determined in soil by using the micro-kjeldahl method (Jackson 1973). The soil available P was extracted using sodium bicarbonate (0.5 M, pH = 8.50) solution according to Olsen *et al.* (1954) method, and measured calorimetrically using the spectrophotometer (Peak Instruments E-2100UV Spectrophotometer, USA). The available potassium (K) in soil was extracted by ammonium acetate (NH_4OAc) solution (1 M) (Carson, 1980), and measured using the flame photometer (ELICO, CL 378 Flamephotometer, UK). The soil properties are given in Table 2.

The prepared soil was artificially contaminated with Cd through soil samples saturating with $Cd(NO_3)_2{\cdot}4H_2O$ (Alpha Chemika CO., India) solutions for producing four contaminated soil samples with gradual increased concentrations of Cd in the following manner: (1) 1 mg Cd Kg^{-1} (Cd1), (2) 10 mg Cd kg^{-1} (Cd10), (3) 100 mg Cd kg^{-1} (Cd100), and (4) 1000 mg Cd Kg^{-1} (Cd1000). After that, the prepared soil samples were left for 3 weeks under laboratory conditions and stirred periodically till drying. Then the contaminated soils were crushed and sieved again for using it in the pot experiment.

Table 2. Some physical and chemical properties of the studied soil.

Property	Unit	Result	Property	Unit	Result
Sand	%	88.15	Total N	mg kg^{-1}	429.33
Silt		4.74	Available P		6.17
Clay		7.11	Available K		126.00
Texture grade		Loamy sand	*SP	%	25.0
pH (1:1 soil:water susp.)	-	7.79	*CEC	cmol kg^{-1}	8.32
EC (1:1 soil:water extr.)	dS m^{-1}	1.19	*OM	%	0.40
Total $CaCO_3$	%	1.83			

***SP = soil saturation percentage, *CEC= cation exchange capacity, *OM= organic matter content.**

In each Cd-contaminated soil, the WC, WCP, PM, and PMP biochars thoroughly mixed with the soil at level of 3% w:w (30 g Kg^{-1}), in addition to a control group that received no biochar. Both the treated and untreated (control) soils in the pots were stored at room temperature and incubated for 30 days under dark conditions. The samples' moisture contents were consistently maintained at field capacity level over the incubation period. After 30 days of incubation, the soils were transferred from the containers into plastic pots. Each pot was filled with one kilogram of each processed soil to produce 60 pots (20 treatments with 3 replicates). Then, the pots were arranged in RCBD (randomized complete block design) in the greenhouse. Phosphorus fertilizer was applied to all pots at a level of 60 Kg P_2O_5 fed^{-1} (143 kg ha^{-1}) in the form of super phosphate fertilizer (15% P_2O_5) before wheat cultivation.

Wheat (*Triticum Sativum*) was used as an experimental crop. Six wheat seeds (Seds 12 local variety) were sown in each pot. The pots were watered to maintain the field capacity moisture level by observing daily weight loss along the experiment period. After 9 days from sowing, thinning was performed carefully by maintaining three healthier plants per pot. The recommended dose of N (150 Kg N fed^{-1} (357 kg ha^{-1}) in the form of ammonium nitrate fertilizer (33.5% N)) and K (50 Kg K_2O fed^{-1} (119 kg ha^{-1}) in the form of potassium sulfate fertilizer (50% K_2O)) was applied to all pots in 2 splits, the 1st was after thinning and the 2nd was after 2 weeks of sowing.

After 45 days from cultivation, the wheat shoots (the above ground biomass) were taken from each pot for measuring the growth parameters, including shoot length (ShL) (cm plant^{-1}) (taken before harvesting directly), shoots fresh weight (FW) (g pot^{-1}), and then the shoots were dried in the drying oven at 70°C until reaching a constant weight and the shoots dry weight (DW) was recorded (g pot^{-1}). The dried shoots were grounded in a stainless-steel mill.

A 0.5 g of the grounded biomass was digested by using H_2SO_4 acid and H_2O_2 according to Chapman & Pratt (1961) method, then the macronutrients (N, P, and K) and Cd concentrations were analyzed for all treatments, using the procedures described by Jackson (1973), in order to evaluate the impact of the various applied biochars on the nutritional status and Cd uptake of the wheat plants. The plant uptake of all determined nutrients by plants was calculated using the following formula:

Nutrient uptake (mg pot^{-1}) = nutrient concentration in plant digest (mg kg^{-1}) * dry weight (g pot^{-1}) /1000

After harvesting, the soil of each pot was well thoroughly mixed and a soil sample was taken from each pot. The soil samples were analyzed for pH (1:1), EC (1:1), organic matter content (%), available P content according to the above-mentioned methods. Moreover, the available Cd in soil samples was extracted by DTPA–triethanolamine (TEA) solution (pH=7.3) according to Lindsay and Norvell (1978) and determined by using an atomic absorption spectrophotometer (Perkin Elmer, A. Analyst 400, USA).

Statistical analysis

For every Cd-contamination level, analysis of variance (ANOVA) was done on all of the results using SPSS version 22 software. Post-hoc comparisons using Duncan's Multiple Range test were done at a significance level of $p \leq 0.05$ (Gomez & Gomez, 1984) to compare the means of the treatments under study with their control treatment.

RESULTS AND DISCUSSION

Biochar characteristics:

Chemical analysis of wood chips and poultry manure derived BC and BCP are shown in Table 1. When BC was modified with P, the pH of WCP- and PMP-BC decreased 0.25 and 0.16 units from the pH of WC- and PM-BC, this decrease may because of the acidic nature of KH_2PO_4 solution. Similar results obtained by Yang *et al.* (2021). The EC of WCP- and PMP-BC BCP was higher (0.784 and 4.42 dS m^{-1}) compared to WC- and PM-BC (0.614 and 4.23 dS m^{-1}) which could be attributed that the addition of KH_2PO_4 introduces potassium and phosphate ions, which can enhance the ionic content of the biochar. This increase in ions leads to higher conductivity (Yang *et al*., 2021).

Total P was about 233.52 and 25027.79 mg kg^{-1} in WC- and PM-BC, which reached to 759.08 and 25793.94 mg kg^{-1} WCP- and PMP-BC, respectively when treated with KH_2PO_4 solution. Similarly, available P was found to be 43.49 and 1385.82 mg kg^{-1} in WC- and PM-BC, while it reached to 375.68 and 1647.29 mg kg^{-1} in WCP- and PMP-BC, respectively. The addition of KH_2PO_4 during the biochar modification process leads to a notable increase in potassium content; the available K content increased from 906 and 1163.33 mg kg^{-1} in WC- and PM-BC to 1589 and 1795 mg kg^{-1} in WCP- and PMP-BC, respectively. Moreover, the higher K content in PM-derived biochar may be due to that the Poultry manure is inherently richer than wood biomass in nutrients, including potassium (Dróżdż *et al*., 2023).

PM- and PMP-BC showed less total C content (68.74 and 66.93 %) and higher N content (3.78 and 3.40 %) compared to it in WC- and WCP-BC, which may be a result of the dietary composition of poultry, which includes protein-rich feeds that contribute to the nitrogen levels in their waste. The PM-derived biochar showed higher values of surface area and total pore volume (6.072 m^2 g^{-1} and 0.08041 cm^3 g^{-1}) than the WC-derived one (4.633 m^2 g^{-1} and 0.07033 cm^3 g^{-1}). And the WCP- and PMP-BC showed lower surface area, total pore volume, and pore size comparing with WC- and PM-BC, this is attributed to the chemical interactions between the phosphate groups and the biochar matrix, which may fill some of existing pores and reduce the overall porosity (Yang *et al*., 2021).

Adsorption isotherms:

Effect of initial concentration (C_o) on adsorption

The adsorption capacity (C_s) (mg g^{-1}) and the Cd^{2+} removal efficiency (%R) by the various produced types of biochar were obviously influenced by the initial concentration of cadmium (C_o). As shown in Figs. 1 and 2, When the initial content of Cd (II) in the solution increased, the adsorption capacity of Cd (II) on all the types of biochar that were investigated increased at a quick rate; the adsorption efficiency decreased with an increase in the initial metal ion concentration. The Cs and % R values of the P-modified BCs were found to be higher than that of the pristine BCs. When the Cd2^{+} initial concentration increased from 1 to 100 mg L^{-1}, the Cd^{2+} adsorption capacity (C_s) of wood chips biochar (WC-BC) increased from 0.470 to 27.98 mg Cd^{2+} g^{-1} with an adsorption percentage (R) of 94.00 to 55.95 % and from 0.488 to 33.35 mg Cd^{2+} g^{-1} with an adsorption efficiency of 97.50 to 66.70% for P-modified wood chips biochar (WCP-BC).

The same trend was obtained when the poultry manure derived biochar was used as an adsorbent for Cd^{2+}ions with higher C_s and %R values. Thus, increasing the Cd^{2+} initial concentration from 1 to 100 Cd^{2+} L^{-1}, the adsorption capacity (C_s) of poultry manure biochar (PM-BC) increased from 0.495 to 46.99 mg Cd^{2+} g^{-1} with a removal efficiency (%R) of 98.90

to 93.98 % and from 0.498 to 48.10 mg Cd^{2+} g^{-1} with an adsorption efficiency of 99.5 to 96.19 % for P-modified poultry manure biochar (PMP-BC). The obtained results demonstrated that increased Cd^{2+} concentrations can produce a greater solute gradient, which provides a driving force to obtain a mass transfer of Cd^{2+} and an equilibrium between the aqueous and the solid phases, drives adsorption on the surface of biochar, and encourages the removal of Cd^{2+} by adsorbents (Usman *et al*., 2016; Huang *et al*., 2020; Wang *et al*., 2022). This explains the increase in adsorption capacity with increasing cadmium concentration in the solution. As initial concentration increases, the ion-exchange matrix of biochar becomes more saturated with Cd^{2+} ions, which may result in less active sites on BCs available to adsorb more ions. This explains the decrease in the Cd^{2+} adsorption efficiency (%R) (Qiu *et al*., 2023).

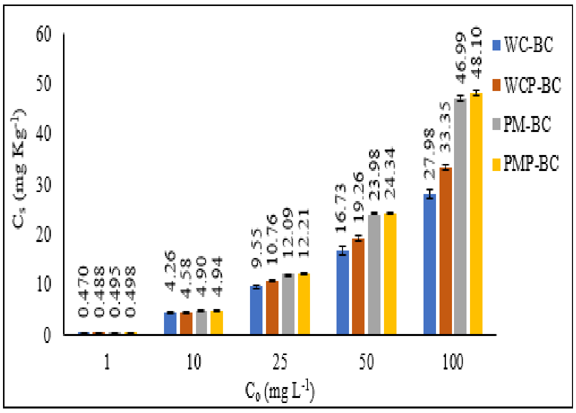

Fig. 1. Effect of the initial Cd concentration in the solution increased on the adsorption capacity of Cd^{2+} on the studied types of biochar (The vertical bars show the standard deviation (SD) values).

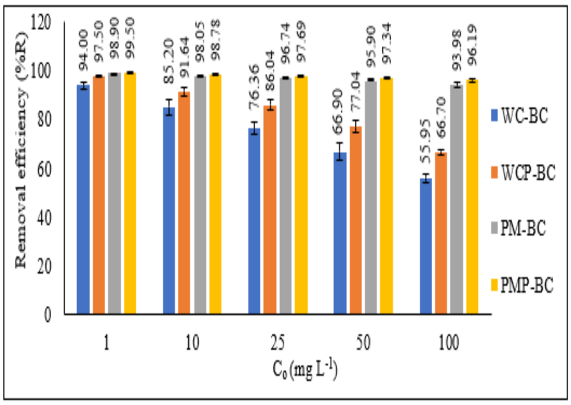

Fig. 2. Effect of the initial Cd concentration in the solution increased on the Cd^{2+} adsorption efficiency of the studied types of biochar (The vertical bars show the standard deviation (SD) values).

To assess the sorption capacities of various BCs, the distribution coefficient (K_d) has been computed for all Cd^{2+} initial concentrations (C_o) (Fig. 3). The Cd^{2+} sorption onto P-modified BCs had the highest K_d values, followed by untreated BCs. From the obtained results, the average of the calculated K_d values is 2.79, 6.15, 20.89, and 38.41 L g^{-1} for WC-, WCP-, PM-, and PMP-BC, respectively. The highest K_d values (99.50 – 12.62 L g^{-1}) were found for Cd sorption by PMP-BC, but the lowest ones (7.83 – 0.64 L g^{-1}) were more pronounced for WC-BC. For all BCs, the values of K_d decreased with the increasing initial concentrations (C_o) of Cd ions. The high K_d value obtained in WCP- and PMP-BC treatments denotes low metal bioavailability due to high metal retention by the solid phase because of chemical interactions. Comparably, a low K_d value obtained in WC- and PM-BC treatments suggests that there is still a significant amount of metal in the solution (Usman *et al*., 2016; Seidou *et al*., 2022). The higher K_d value obtained in the experiment with lower Cd^{2+} initial concentrations is associated with the high selectivity of the sorption sites, which have relatively strong bonding energies. Otherwise, at higher initial concentrations, Cd^{2+} sorption becomes non-specific as the particular bonding sites get progressively occupied, leading to lower K_d values (Bian *et al*., 2022).

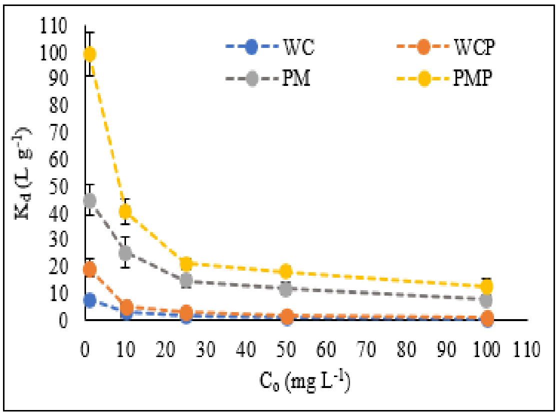

Fig. 3. Effect of the initial Cd^{2+} concentration on the distribution coefficient (K_d) of Cd^{2+} adsorption on the studied types of biochar (The vertical bars show the standard deviation (SD) values).

Figure 4 illustrates the Cd^{2+} ion sorption isotherms onto the types of biochar that were studied. The adsorption isotherms show how the adsorption capacity (Cs) (mg g^{-1}) of the Cd^{2+} ions at the equilibrium concentration (C_e) (mg L^{-1}) varies for WC-BC, WCP-BC, PM-BC, and PMP-BC. WC-BC and WCP-BC exhibit different adsorption isotherm patterns in comparison to PM-BC and PMP-BC. Regarding to the adsorption isotherms of WC-BC and WCP-BC, it can be noticed that at lower initial concentrations, the curves have a relatively high slope, whereas at higher ones, they show a relatively low slope. The Cd (II) sorption onto WC-BC and WCP-BC tends to be an L-shaped isotherm. Such adsorption behavior could be explained by the high affinity and high Cd^{2+} adsorption efficiency of WC-BC and WCP-BC at low Cd^{2+} initial concentrations. However, they decrease as Cd^{2+} initial concentration increases. Saravanakumar *et al*. (2021) reported similar results for the adsorption of Pb^{2+} and Cd^{2+} by date seed-derived biochar. And in another study, the adsorption isotherm data for Cd^{2+} by pristine and phosphate modified BCs from apple tree branches were found to be L-shaped (Wang *et al*., 2022).

As for PM-BC and PMP-BC, their adsorption isotherms behavior for Cd^{2+} ions is characterized by a "H" type (high-affinity isotherm) with a high slope for all investigated concentrations, confirming the high affinity of cadmium even at higher initial concentrations. And the active binding sites for Cd (II) sorption onto PM and PMP-BCs are still available for a further additional adsorption. This indicates that PM-BC and PMP-BC are more effective than WC-BC and WCP-BC for adsorbing and removing Cd^{2+}

from contaminated water and aqueous solutions, even at high Cd^{2+} contamination levels.

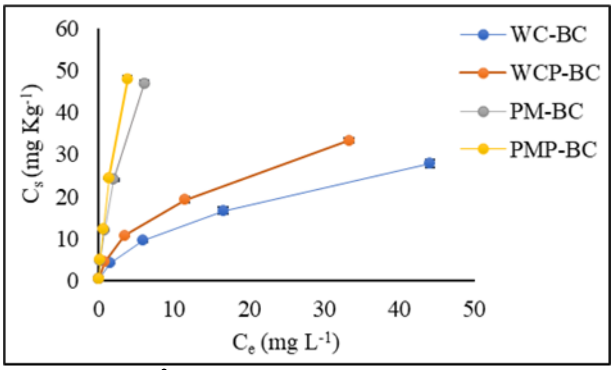

Fig. 4. The Cd^{2+} ion sorption isotherms onto the studied types of biochar (The vertical bars show the standard deviation (SD) values).

Adsorption Isotherms and Models

Table 3 showed the parameters of the linear regression of the Langmuir, Freundlich, and Temkin isotherm model equations. The suitability of the three adsorption isotherm models for representing Cd^{2+} adsorption by the examined BCs declines in the following order: Freundlich > Langmuir >> Temkin isotherm, according to the coefficient of determination (R^2) values that were obtained for each model. For all BCs, the R^2 values of Freundlich model were greater than 0.95 (0.9962–0.9988), which were much higher than those of Langmuir model (0.8212–0.9367) and Temkin model (0.7058 - 0.7966). The higher determination coefficient (R^2) obtained values of the Freundlich isotherm compared to the other two tested models indicate that the adsorption process was controlled by the surface diversification and the exponential distribution of BCs' active sites (Idrees *et al*., 2016). This means that the BCs may have a heterogeneous surface with variable affinities for Cd^{2+} and the different sites on these BCs interact with Cd^{2+} differently, and there was multilayer Cd^{2+} adsorption on the BC surface (Khayyun and Mseer, 2019) with varied adsorption energy across the different sites. This could be due to the presence of functional groups or variations in the characteristics of the BCs' surfaces, leading to different adsorption energies (Vitek and Masini, 2023). Similar studies found that Freundlich model fitted the heavy metal by the conocarpus wastes-derived biochar for Fe^{+2} adsorption (Usman *et al*., 2013), the chicken manure Biochar (Huang *et al*., 2020), and the woody agricultural wastes biochar (Li *et al*., 2022).

The estimated maximum Cd^{2+} sorption capacity (Q_m) in the Langmuir adsorption isotherm under the studied Cd concentrations is 294.12, 344.82, 555.56, and 588.24 mmol Kg^{-1}, these values correspond to 33.06, 38.76, 62.45, and 66.13 mg g^{-1} biochar for WC-BC, WCP-BC, PM-BC, and PMP-BC, respectively (Table 3). Comparing between the pristine biochar and P-modified biochar, the adsorption energy coefficient (affinity index) (b) calculated from the Langmuir adsorption isotherm of Cd^{2+} increased from 11.33 L $mmol^{-1}$ for WC-BC to 14.50 L $mmol^{-1}$ for WCP-BC, and from 45.00 L $mmol^{-1}$ for PM-BC to 56.67 L $mmol^{-1}$ for PMP-BC.

Table 3. Adsorption isotherms constants for Cd adsorption by the studied types of biochar.

Biochar	Langmuir adsorption isotherm constants			Freundlich adsorption isotherm constants			Temkin adsorption isotherm constants		
(BC) type	Q_m (mmol kg^{-1})	B (L $mmol^{-1}$)	R^2	K (L kg^{-1})	1/n	R^2	B_T (J mol^{-1})	K_T (L $mmol^{-1}$)	R^2
WC	294.12 *(33.06)	11.33	0.9331	494.08	0.622	0.9962	0.0337	774.97	0.7966
WCP	344.83 *(38.76)	14.50	0.9367	671.58	0.590	0.9968	0.0368	1578.34	0.7819
PM	555.56 *(62.45)	45.00	0.8878	3772.25	0.723	0.9974	0.0585	3554.85	0.7416
PMP	588.24 *(66.13)	56.67	0.8218	4400.48	0.687	0.9988	0.0552	7294.88	0.7058

***The values between brackets represent the Q_m values in mg Cd g^{-1} biochar.**

The adsorption capacity constant (K_f) fitted by the Freundlich model of WC-BC, WCP-BC, PM-BC, and PMP-BC are 494.08, 671.58, 3772.25, and 4400.48 L Kg^{-1}, respectively. This reflects the higher adsorption capacity (K_f) of P-treated biochars (WCP-BC and PMP-BC) than the raw one. The constant 1/n value that offers valuable perspectives on the sorption intensity and favorability varied between 0.590 and 0.723 (Table 3), which 1/n values between 0 and 1 indicating favorable adsorption conditions for Cd^{2+} (Huang *et al*., 2020).

The ability of wood chips and poultry manure biochars to remove cadmium from aqueous solutions and polluted water is due to several mechanisms, including: (a) precipitation or co-precipitation through production of precipitates of Cd-(hydr)oxide, -carbonate, or -phosphate; (b) electrostatic interactions between metal cations and the activated functional groups; (c) surface chemisorption between the d-electrons of metals and the delocalized π-electrons of chars. (d) surface complexation with oxygen- and nitrogen-containing functional groups, thus the phenolic -OH and -COOH as well as the C=N groups that are present on the surface of biochar may be the cause of adsorption. And the electronegative O and N atoms or the π-electrons of aromatic functional groups may also be the cause of Cd adsorption; and (d) the cation exchange mechanism through alkali earth cations (Ca and Mg) releasing from biochar and the free available sites replacing by Cd creating a new bond. Similar attributes were displayed by Chen *et al*. (2019), Usman *et al.* (2016). Also, insoluble precipitates of cadmium carbonate are produced when carbonate ions (CO_3^{-2}) in the biochar combine with Cd ions. Roughly 73.7% of the total removal efficiency is accounted for by this process (Liu *et al*., 2021; Ge *et al*., 2024). Furthermore, biochar's aromatic structures promote cation-π interactions, giving Cd ions more places to bind.

The higher efficiency of PM-derived biochars in reducing the availability of Cd might be due to its large surface area and cation exchange capability through adsorption and complexation. Complexation processes on the surface of the biochar may result in the formation of novel less soluble compounds after adsorption, including cadmium hydroxide ($Cd(OH)_2$) and cadmium sulfide (CdS) (Wang *et al*., 2024). The higher pH in the PM and PMP-biochar treated soils enhances the immobilization of Cd by promoting the formation of less soluble $Cd(OH)_2$ compound, which decreased its availability for wheat plants uptake (Xu *et al*., 2022; Zhang *et al*., 2024).

It is noticeable that the P-treated biochar samples (WCP-BC and PMP-BC) had higher values of adsorption maxima (Q_m), bonding energy coefficients (b), sorption capacity (K_f) and sorption intensity (n) than those for untreated biochar samples (WC-BC and PM-BC). These findings imply that treating biochar with P increased the Cd^{2+} sorption capacity of these biochars significantly. This may be due to that the phosphate addition to biochar increases the availability of P ions, which can react with cadmium ions in the solution. As a result, cadmium phosphate precipitates $Cd_3(PO_4)_2$, which is a low solubility product that effectively immobilizes cadmium and decreases its environmental solubility as well as its ability to be extracted from aqueous solutions. This precipitation process happens when sufficient phosphorus is added to the soil. However, studies suggest that under low cadmium concentrations, this precipitation might not occur efficiently (Ruangcharus *et al*., 2020). Biochar can more easily form complexes with Cd^{+2} when it has been loaded with phosphorus. Treating biochar with KH_2PO_4 may cause phosphate ions to develop on the surface of the biochar, these ions interact with the functional groups on the biochar surface, increasing the surface's total negative charge and facilitating a larger uptake of positively charged cadmium ions. The P-treated biochar by forming coordination bonds with Cd through functional groups like P=O and P=OOH via filling empty orbitals (Qiu *et al*., 2023). These stable complexes formation can enhance Cd^{+2} remediation in polluted soils. Moreover, the cation–π bond in P-loaded biochar between Cd^{2+} and the π-electron donor affects the overall process of removing heavy metals from aqueous solutions in addition to influencing the binding affinity. These explanations are matching with what Chen *et al*. (2019), Ruangcharus *et al*. (2020), Qiu *et al*. (2023), and Yu *et al*. (2024) showed.

The pot experiment:

Soil pH, EC, and OM:

Soil pH, EC, and soil OM content affected with addition of biochar types to Cd- polluted soils (Fig. 5). The average of Soil pH increased from 7.71 in control contaminated soils to 7.87, 7.82, 8.07, and 8.00 in WC-, WCP-, PM-, and PMP-treated soils, respectively with an increase of 0.16, 0.11, 0.36, and 0.29 units of control soil pH, respectively. The increase in soil pH that observed after application of BCs especially derived from poultry manure may be related to its ash content, which contains basic cations that can increase soil pH (Masocha & Dikinya, 2022). The addition of both types of biochar led to a significant increase in the average soil EC values from 1.45 dS m^{-1} in the control soil to 1.71, 1.81, 3.10, and 3.18 dS m^{-1} in WC-, WCP-, PM-, and PMP-biochar treatments, respectively. This increase is frequently attributed to the existence of soluble salts. Poultry manure biochar (PM-BC) typically contains higher concentrations of the soluble nutrients, which increase EC when applied to soils. Similar findings were obtained by Sun *et al*. (2024), Joardar *et al*. (2020). In comparison, wood biochar's (WC-BC) composition results in a lower potential for nutrients and salts release. On average, amending soil with WC, WCP, PM and PMP biochar enhanced significantly the soil OM (%) by 1.95, 1.78, 7.16, and 7.11 times, respectively as compared to the nontreated controls. This improvement in soil OM content could be due to the wood biochar is indeed composed of lignin and cellulose which are stable and resistant to microbial decomposition, which is vital for preserving the soil fertility and structure as well as carbon sequestration (Domingues *et al*., 2017). In comparison to untreated control soils, Adekiya *et al*. (2020) found that applying 15 Mg ha^{-1} of hardwood biochar over a two-year period increased SOM by an average of 138 %. The greatest effect of poultry manure-derived biochar in OM increased may be related to that the higher organic matter content of poultry manure biochar than that of wood biochar. Studies have shown values as high as 39.47% for poultry manure biochar produced at 475 °C (Dróżdż *et al*., 2023). This biochar is known to play a major role in improving soil fertility and quality.

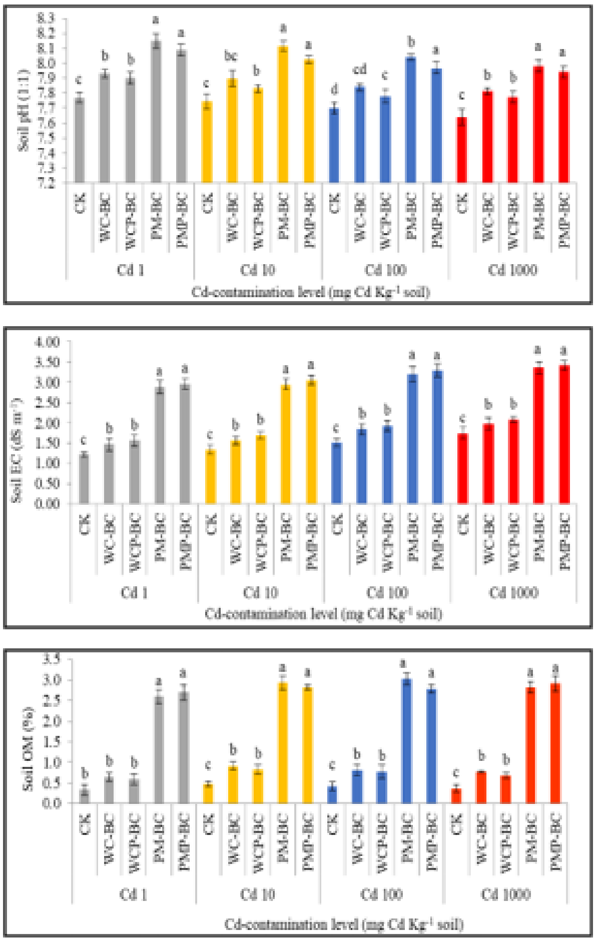

Fig. 5. Effect of biochar types (WC, WCP, PM, and PMP) on soil pH, electrical conductivity (EC) and organic matter (OM) content in the Cd-contaminated soils. Each value is the mean of three replicates and the vertical bars indicates the standard deviation. Significant differences between treatments of every Cd level are shown by different lowercase letters on each bar based on the Duncan's Multiple Range test at $p \leq 0.05$.

Available phosphorus (P) in soil:

Results presented in Fig. 6 indicate that the soil available P increased significantly by application of WCP-, PM- and PMP-BCs comparing to the control and WC-biochar amended ones under all the studied levels of contamination with Cd. The average of soil available P increased from 6.62 mg kg^{-1} in control soils to 12.95, 47.09, and 49.73 mg kg^{-1} in WCP-, PM-, PMP-biochar treated soils, respectively and non-significantly to 7.52 mg kg^{-1} in WC-BC amended ones. The high content of available and total phosphorus in poultry manure biochar compared to wood one is the reason for the increase in available phosphorus in the soil treated with poultry manure biochar. Sikder & Joardar (2019) indicated that poultry manure biochar with level of 4 t ha^{-1} increased soil available P from 37 mg kg^{-1} in control to 52.40 mg P kg^{-1}.The positive effect for WCP- and PMP- BCs on the soil available P because the treatment with KH_2PO_4 leads to a substantial increase in their available phosphorus content, these results agreed with Ahmad *et al.* (2018) and Ng *et al.* (2022) who found that application of P-enriched biochar enhanced the available P in soil.

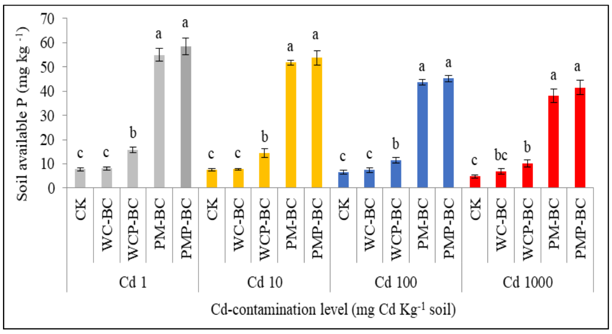

Fig. 6. Effect of biochar types (WC, WCP, PM, and PMP) on soil available phosphorus (P) ($NaHCO_3$-extractable P) content in the Cd-contaminated soils. Each value is the mean of three replicates and the vertical bars indicates the standard deviation. Significant differences between treatments of every Cd level are shown by different lowercase letters on each bar based on the Duncan's Multiple Range test at $p \leq 0.05$.

DTPA-extractable Cd in soil:

Results shown in Fig. 7 indicated that the concentrations of plant-available Cd (DTPA-extractable Cd) varied significantly across all biochar treatments compared to control. These findings demonstrated how biochar may be able to lessen the negative impacts of Cd on plant growth in contaminated soil. Under application of WC, WCP, PM, and PMP, the DTPA-extractable Cd decreased to 0.300, 0.263, 0.144, 0.125 mg kg^{-1} soil, respectively from 0.869 mg kg^{-1} in control in Cd1-treated soil (by a decrease of 65.53, 69.71, 83.46, and 85.65 %). While in Cd10-treated soil, the DTPA-extractable Cd decreased significantly from 3.77 mg kg^{-1} in control soil to 1.73, 1.46, 0.88, and 0.82 mg kg^{-1} soil in WC-, WCP, PM, PMP-BC amended soil, respectively (by a decrease of 54.11, 61.27, 76.62, and 78.22%). On the other hand, biochar addition to the Cd100-spiked soil showed a significant reduction in DTPA-extracted Cd from 20.88 mg kg^{-1} in control to 13.43, 12.31, 8.96, and 8.03 mg kg^{-1} in WC-, WCP-, PM-, and PMP-BC treated soil, respectively with a decrease percentage of 35.69, 41.04, 57.11 and 61.56 %. In the case of Cd1000-polluted soil, the DTPA-extractable Cd from soil recorded a reduction by 13.96, 15.31, 33.89, and 37.95 % compared to control where it decreased from 645.67 mg kg^{-1} in control soil to 555.50, 546.83, 426.83, and 400.67 mg kg^{-1} under application of WC-, WCP-, PM-, and PMP-biochar, respectively. The obvious reduction in the DTPA-extractable Cd and Cd uptake in wheat plants indicate that wood chips- and poultry manure-derived biochars whether in raw or P-treated form are effective in the immobilization of heavy metals like Cd in contaminated soils even though this effectiveness can vary depending on biochar type. This immobilization ability could be attributed to several mechanisms that were previously explained in detail in 3.2.2 section. Our findings are matched with those of Beesley *et al.* (2010) who observed that the incubation of contaminated soil with hardwood biochar for 56 days considerably decreased the concentration of Cd. According to a meta-analysis that assessed various types of biochar, applying wood biochar has been shown to lower soil Cd availability by about 62.88%, and the biochar applying rates of 2 to 3 % can optimize its ability to lower soil Cd levels, decrease their mobility, enhance soil health, lower plant uptake of Cd, and improve plant health and biomass (Lu *et al.*, 2022; Liu *et al.*, 2021). Similar results were obtained by Antonangelo *et al.* (2023) who found that addition of switchgrass- and poultry litter-derived biochars dramatically reduced the uptake of zinc (Zn), lead (Pb), and cadmium (Cd) by ryegrass in contaminated soils.

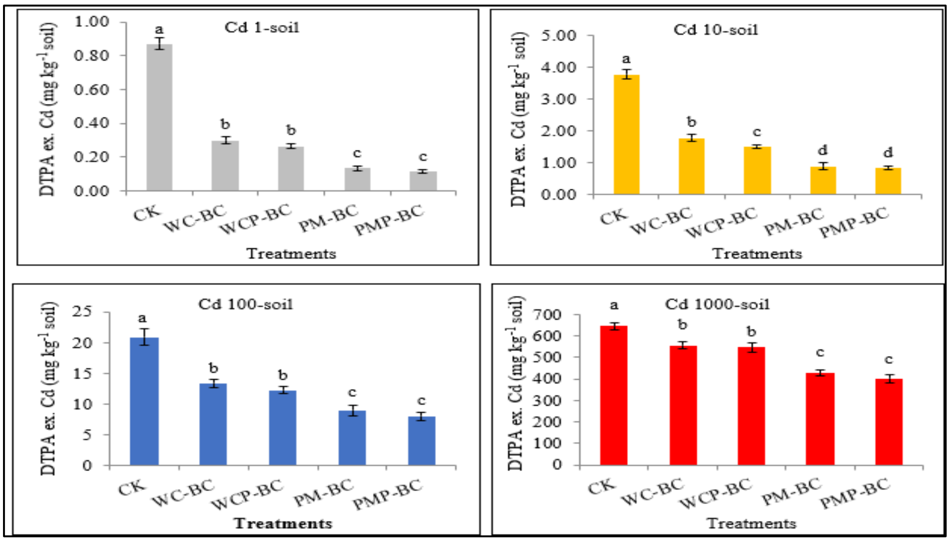

Fig. 7. Effect of biochar types (WC, WCP, PM, and PMP) on DTPA-extractable Cd from the different Cd-contaminated soils. Each value is the mean of three replicates and the vertical bars indicates the standard deviation. Significant differences between treatments of every Cd level are shown by different lowercase letters on each bar based on the Duncan's Multiple Range test at $p \leq 0.05$.

Wheat plants growth parameters

A reduction in wheat plants growth with increasing of Cd level was observed in the results, which may be due to the Cd toxicity to plant which adversely affects photosynthetic processes by inhibiting chlorophyll synthesis, altering chloroplast function, and reduce biomass production (Zhao *et al.*, 2021).

Amending the Cd-contaminated soil with biochar resulted in significant enhancement in the plant growth indices (Fig. 8). In the Cd1-spiked soil, the shoot fresh weight (FW) increased significantly from 6.03 g pot^{-1} in control to 10.52, 12.09, 17.44, and 18.31 g pot^{-1} in WC, WCP, PM, and PMP-treated pots, respectively; by 74.36, 100.33, 189.01, and 203.43% more than control, respectively. While in the Cd10-spiked soil, the shoot FW increased from 3.91 g pot^{-1} in control to 6.26, 7.05, 10.54 and 11.23 g pot^{-1} in WC, WCP, PM, and PMP- treated pots, respectively; by 60.05, 80.15, 169.42, and 187.05% more than control, respectively. Similar significant improvement in shoot FW from 2.09 g pot^{-1} in control treatment of Cd100-spiked soil to 3.08, 3.31, 5.20, and 5.78 g pot^{-1}; by 47.42, 58.37, 149.02, and 176.59% more than control under application of WC, WCP, PM, PMP types of biochar, respectively. Another significant increase was obtained in the plant shoot FW under Cd1000-spiked soil level from 0.81 g pot^{-1} in control treatment to 1.08, 1.16, 1.84, 2.03 g pot^{-1} under WC-, WCP-, PM-, and PMP-BC application by 33.33, 43.21, 127.16, and 150.62 % more than control, respectively.

The shoot dry weight improved significantly from 2.83 g pot^{-1} in control treatment to 4.59, 5.15, 6.31, and 6.60 g pot^{-1}, (by 61.81, 81.80, 122.60, and 132.95 % more than control) in WC-, WCP-, PM-, PMP-biochar amended treatments under application of Cd1 level of Cd. However, in Cd10-spiked soils, there was a significant increase in shoot DW from 1.89 g pot^{-1} in control to 2.92, 3.36, 3.92, and 4.05 g pot^{-1} (by 54.50, 77.60, 107.58, 114.29 % more than control) under application of WC-, WCP-, PM-, and PMP-BC, respectively. Similar trend was observed in the Cd100- and Cd1000-spiked soils, where the shoot DW increased from 1.17 and 0.50 g pot^{-1} in control treatments, respectively to 1.74, 1.84, 2.12, and 2.30 g pot^{-1} (by 49.43, 57.43, 81.71, 96.86 % more than control of Cd100-spiked soil) and to 0.64, 0.69, 0.87, and 0.93 g pot^{-1} (by 27.15, 37.09, 72.85, and 85.43% more than control of Cd1000-spiked soil) in the amended soils with WC-, WCP-, PM-, and PMP-BCs, respectively (Fig. 8).

The shoot length (ShL) decreased by increasing the level of soil pollution with Cd from 28.19 cm plant^{-1} in Cd1-spiked soil to 27.03, 24.62, and 16.04 cm plant^{-1} in Cd10-, Cd100-, and Cd1000-spiked soil, respectively. Addition of WC-, WCP-, PM-, and PMP-biochar significantly increased the plant shoot length (ShL) by an increase of 15.88, 20.85, 28.77, and 34.80% in Cd1-polluted soil, by 11.34, 17.79, 27.50, 31.41% in Cd10-polluted soil, by 7.31, 11.45, 24.10, 25.76% in Cd100-contaminated soil, and by 6.03, 9.23, 21.61, and 23.42% in Cd1000-contaminated soil more than control, respectively (Fig. 8).

The obtained improvement in wheat plants growth in our study may be not only attributed to the reducing toxic Cd bioavailability and uptake but also to the effects of biochar in improving soil properties, nutrient availability which collectively exhibit healthier plants. biochar improves the cation exchange capacity and soil porosity, which aid in the retention of nutrients and moisture (Murtaza *et al.*, 2024). Moreover, biochar has the ability to increase soil microbial activity, promoting a healthier environment that promotes plant growth (Agarwal *et al.*, 2022). Our results agreed with Zha *et al.* (2022) who found that soil-applied bamboo wood biochar (1.0% w/w) with zinc oxide nanoparticles (ZnO NPs) foliar spray increased maize growth and significantly decreased Cd and Zn accumulations in the grains of maize under Cd-contaminated soil. Similar studies proved that PM biochar promotes growth and lessens the phytotoxic effects of heavy metals; Ijaz *et al.* (2020) discovered that adding PMB reduced wheat's uptake of Cd by causing Cd immobilization in alkaline-polluted soil. In lead (Pb)-contaminated soil tests, the addition of chicken manure and biochar greatly increased maize growth while lowering Pb uptake. In comparison to control groups, the treatments resulted in a 69.63% increase in dry weight and a 43.23% rise in plant height (Liu *et al.*, 2021). Haider *et al.* (2022) indicated that co-application of poultry manure biochar with some beneficial microorganisms to calcareous sandy loam soil has been found to reduce Cd accumulation and enhance maize growth.

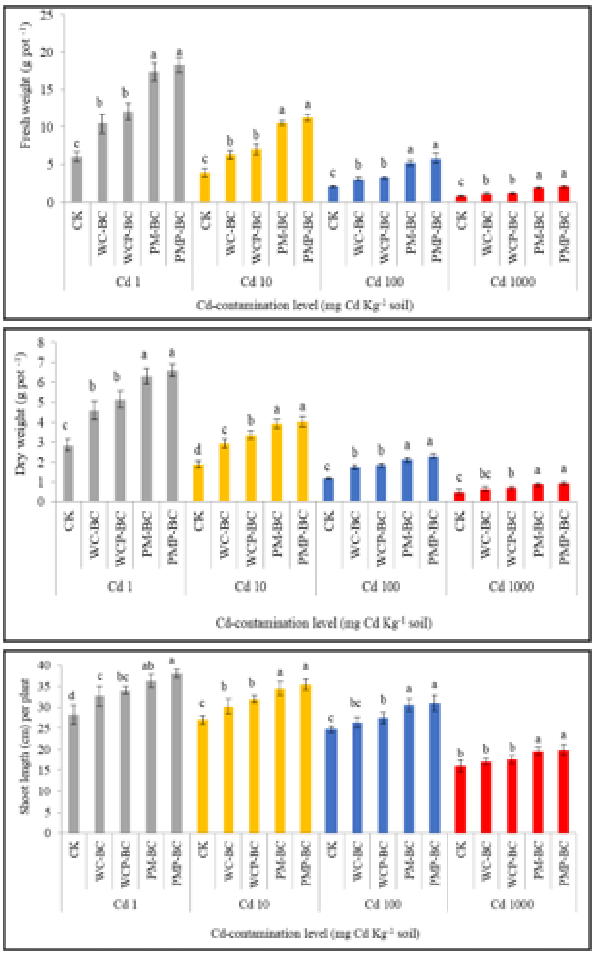

Fig. 8. Effect of biochar types (WC, WCP, PM, and PMP) on shoots fresh weight (g pot^{-1}), shoots dry weight (g pot^{-1}), and shoot length (cm plant^{-1}) of wheat plants under different Cd-contaminated soils. Each value is the mean of three replicates and the vertical bars indicates the standard deviation. Significant differences between treatments of every Cd level are shown by different lowercase letters on each bar based on the Duncan's Multiple Range test at $p \leq 0.05$.

The obtained results showed a higher effect for P-treated biochars reducing Cd availability to wheat plants compared to untreated BCs with P. This may be due to the role of phosphorus in forming cadmium phosphate precipitate and reducing the availability of cadmium to plants (Ahmad *et al*., 2018). Also, Ding *et al*. (2022) found that in a sandy loam soil contaminated with Cd, Pb, Zn, and Cu, the P-loaded biochar increased tomato growth and yield by 37% more than control.

Nutrients (N, P, and K) content and uptake

It was observed that N, P, and K contents and uptakes in wheat plants decreased with increasing the level of Cd, mainly due to the ability of Cd bind directly to the membranes of root cells, blocking the channels that allow nutrients uptake, harm cellular structures, interfere with nutrient transport pathways, thus reducing the ability of plant to absorb the essential nutrients and growth (Sperdouli, 2022). Biochar applications resulted in significant increase in the N, P, and K concentrations and uptakes in wheat plants (Table 4). The N uptake increased significantly from 114.68 mg pot^{-1} in control to 195.35, 216.15, 290.62, and 326.46 mg pot^{-1} with addition of WC-, WCP-, PM-, and PMP-BC, respectively in the Cd1-spiked soil, by an increase of 70.34, 88.48, 153.42, and 184.67%, respectively. For the Cd10-polluted soil, the applying of WC-, WCP-, PM-, and PMP-biochar enhanced the N uptake to 114.10, 129.40, 169.37, and 181.28 mg pot^{-1} comparing with control treatment (70.17 mg pot^{-1}); by an increase of 62.61, 84.41, 141.37, and 158.34%, respectively. Application WC-, WCP-, PM-, and PMP-biochar types caused significant improvement in N uptake from 41.34 mg pot^{-1} in control to 62.52, 66.65, 89.20, 93.74 mg pot^{-1} by an increase of 51.23, 61.18, 115.77, and 126.75 %, respectively for the Cd100-treated soil and from 10.36 mg pot^{-1} in control to 15.10, 17.16, 21.67, and 22.83 mg pot^{-1} by an increase of 45.75, 65.64, 109.17, and 120.27 %, respectively for the Cd1000-treated soil.

Amending soil with the different investigated biochars especially PM- and PMP-BCs enhanced P concentration and uptake. In the Cd1-contaminated soil, the P uptake increased significantly to 17.87, 22.03, 48.48, and 51.52 mg pot^{-1}, respectively; by 74.34, 114.93, 372.98, and 402.63 % more than control treatment (10.25 mg pot^{-1}). The improvement in P uptake by wheat plants in Cd10-treated soil was by 66.17, 102.46, 356.49, and 390.31 %, respectively more than P uptake of control plants (6.09 mg pot^{-1}) (Table 4). Similar trend was observed under Cd100- and Cd1000-polluted soils, the P uptake increased by 63.29, 95.37, 297.69, and 317.34% and by 50.88, 81.58, 232.46, and 240.35% more than control treatments after amending of Cd100- and Cd1000-spiked soils with WC-, WCP-, PM-, and PMP-BC, respectively. As noticed from our results, the P-treated biochar treatments showed an increase in P concentration and uptake in wheat plants which correlated with high available P content in soil that amended with these BCs. Wali *et al*. (2022) found that using P-enriched biochar made from wheat straw feedstock to amend sandy clay loam soil improved the microbial population, raised the amount of P accessible in the soil, and accelerated maize growth and P uptake.

Under contamination level of Cd1, the increase in K uptake by wheat plants in the WC-, WCP-, PM-, PMP-BC treated soils was higher than control by 68.58, 96.29, 265.88, and 275.77 %, respectively. Also, in Cd10-spiked soil, a significant enhancement was observed in K uptake from 63.77 mg pot^{-1} in control to 104.15, 116.45, 215.69, 226.91 mg pot^{-1} after amending that soil with WC-, WCP-, PM-, PMP-BC, respectively. The wheat plants of Cd100- and Cd1000-treated soils recorded the lowest K uptake values (35.30 and 8.62 mg pot^{-1}), which increased significantly to 55.86, 58.04, 114.96, and 120.10 mg pot^{-1} and to 10.82, 13.51, 27.03, and 28.36 mg pot^{-1} in WC-, WCP-, PM-, and PMP-BC amended soils under both two Cd levels, respectively (Table 4). Incorporation of wood- and poultry manure- biochar, whether in their raw or in the P-modified form, led to a clear improvement in the uptake of N, P, and K nutrients in wheat plants under all levels of Cd contamination. Previous studied showed that nitrogen availability for plants can be increased by combining wood biochar with N fertilizers, which can significantly minimize nitrogen losses through leaching and volatilization and enhance N uptake by plant (Maroušek & Trakal, 2022). Moreover, biochar can act as a slow-release K fertilizer, the dissolved K is released into the soil quickly at first, and then its concentration decreases as the residual K slowly releases from the biochar matrix (Premalatha *et al*., 2023). This dynamic provides a continuous supply of K, which supports ongoing plant growth. In a previous study, Amin (2023) proved that wood chips biochar at level of 2.5% increased the soil total available nitrogen and available K by 30.1% by 19%, respectively and increased the N, P, and K uptake of red radish plant by 50, 120, and 90 %, compared to the unamended treatment.

Our results indicated a greater impact for PM biochar than WC one on enhancement nutrients uptake by wheat, that because of the Poultry manure (PM) is rich in essential nutrients such as N, P, K, Ca, and Mg, (about 5.52% to 8% N, 0.9–3.5% P and 1.5–3% K of its dry weight) which are essential for plant growth (Dróżdż *et al*., 2023). When converted into biochar through pyrolysis, the nutrient profile can be improved, become richer in these nutrients, more stable and readily available for plant uptake, so PM-derived biochar acts as an excellent soil amendment, boosting soil fertility increasing SOM, improving the sandy textured- soil CEC, and promoting nutrients uptake (Mohamed & Hammam, 2019). Similar study by Agbede *et al*. (2024) approved that the combined addition of wood biochar (30 t ha^{-1}) with poultry manure (10 t ha^{-1}) increased the contents of K by 123.8%, P by 416.7%, and N by 88.2% comparing with control in sweet potato leaves.

Cadmium (Cd) concertation and uptake in wheat plants

The concentration and uptake of Cd in wheat shoots are illustrated in Table 4. Results indicated that the Cd concentration decreased significantly as a result of amending soil with the studied biochars in comparison with control treatments under all the studied levels of contamination with Cd. In Cd1-treated soil, applying of WC, WCP, PM, and PMP biochars decreased the Cd concentration significantly from 32.67 mg kg^{-1} in control to 14.06, 10.64, 6.73, and 5.77 mg kg^{-1}, respectively; by a decrease of 56.97, 67.44, 79.41, and 82.33 %, and decreased the Cd uptake of wheat plants from 92.28 µg pot^{-1} (30.76 µg plant^{-1}) in control to 64.23, 54.41, 42.26, and 37.86 µg pot^{-1} (21.41, 18.14, 14.08, and 12.62 µg plant^{-1}), respectively; by a decrease of 30.40, 41.04, 54.21, and 58.99 %. Under application of Cd10 level of contamination, biochars addition reduced the Cd concentration in wheat shoots significantly to 20.15, 17.22, 12.02, and 10.24 mg kg^{-1} in the WC-, WCP-, PM-, and PM-amended soil, respectively by a decrease of 53.62, 60.37, 72.34, and 76.44 % less than control treatment (43.46 mg kg^{-1}), also the Cd uptake decreased significantly from 81.75 µg pot^{-1} (27.25 µg plant^{-1}) in control to 58.44, 57.59, 47.24, and 41.64 µg pot^{-1} (19.48, 19.19, 15.75, and 13.88 µg plant^{-1}) as a result of amending soil with WC-, WCP-, PM-,PMP-biochar, respectively; by a reduction percentage of 28.52, 29.54, 42.21, 49.06 % (Table 4). In the Cd100-treated soil, a significant reduction was observed in Cd concentration values from 61.27 mg kg^{-1} in control treatment to 37.67, 32.13, 21.91, and 18.79 mg kg^{-1} in WC-, WCP-, PM-, and PMP-biochar treated plants, respectively; by a reduction of 38.52, 47.56, 64.24, and 69.34 %. Furthermore, the wheat plants uptake of Cd in the Cd100-treated soil decreased significantly from 71.41 µg pot^{-1} (23.80 µg plant^{-1}) in control treatment to 65.39, 58.68, 46.25, and 42.83 µg pot^{-1} (21.79, 19.56, 15.42, 14.28 µg plant^{-1}), respectively in the WC-, WCP-, PM-, and PMP-biochar amended soil, respectively; by a decrease percentage of 8.42, 17.82, 35.23, and 40.03 %.

A similar trend was recorded in the Cd1000-spiked soil, where the Cd concentration recorded a significant reduction from 109.86 mg kg^{-1} in the control plants to 82.65, 75.40, 46.26, and 42.38 mg kg^{-1} WC-, WCP-, PM-, and PMP-biochar amended plants, respectively, by a decrease percentage of 24.76, 31.37, 57.89, and 61.42%. Moreover, the Cd uptake of wheat plants under application of Cd1000 level of contamination decreased non-significantly from 55.23 µg pot^{-1} (18.41 µg plant^{-1}) in control to 52.42 and 50.72 µg pot^{-1} (17.47 and 16.91 µg plant^{-1}) in the WC- and WCP-biochar amended plants by a decrease percentage of 5.10 and 8.17%, and significantly to 40.32 and 39.49 µg pot^{-1} (13.44 and 13.16 µg plant^{-1}) in PM- and PMP-biochar amended ones by a decrease percentage of 27.0 and 28.50%, respectively (Table 4).

Table 4. Effect of biochar types (WC, WCP, PM, and PMP) on N, P, K, and Cd concentrations and uptakes of wheat plants under different Cd-contaminated soils.

Cd level	Treat.	N conc. (%)	N uptake (mg pot^{-1})	P conc. (%)	P uptake (mg pot^{-1})	K conc. (%)	K uptake (mg pot^{-1})	Cd conc. (mg Kg^{-1})	Cd uptake (µg pot^{-1})	Cd uptake (µg plant^{-1})
Cd1	CK	4.05 b±0.07	114.68 e±11.19	0.36 b±0.02	10.25 c±1.22	3.57 e±0.04	101.04 c±9.79	32.67 a±2.01	92.28 a±6.18	30.76 a±2.06
	WC-BC	4.27 b±0.19	195.35 d±12.83	0.39 b±0.02	17.87 b±1.35	3.72 d±0.04	170.33 b±15.07	14.06 b±1.96	64.23 b±8.39	21.41 b±2.80
	WCP-BC	4.22 b±0.28	216.15 c±5.97	0.43 b±0.03	22.03 b±2.17	3.84 c±0.04	197.33 b±14.45	10.64 c±1.50	54.41 bc±4.00	18.14 bc±1.33
	PM-BC	4.61 a±0.19	290.62 b±6.69	0.77 a±0.04	48.48 a±5.02	5.86 a±0.07	369.69 a±17.36	6.73 d±1.47	42.26 cd±8.15	14.08 cd±2.71
	PMP-BC	4.95 a±0.11	326.46 a±9.15	0.78 a±0.08	51.52 a±2.11	5.75 b±0.05	379.68 a±16.75	5.77 d±1.37	37.85 d±7.27	12.62 d±2.42
Cd10	CK	3.72 b±0.11	70.17 e±8.25	0.32 b±0.02	6.09 c±0.52	3.38 c±0.04	63.77 c±6.39	43.46 a±2.66	81.75 a±5.36	27.25 a±1.79
	WC-BC	3.92 b±0.13	114.10 d±4.16	0.35 b±0.02	10.12 b±1.05	3.58 b±0.05	104.15 b±5.84	20.15 b±2.61	58.44 b±4.29	19.48 b±1.43
	WCP-BC	3.86 b±0.09	129.40 c±4.67	0.37 b±0.03	12.33 b±1.55	3.47 bc±0.10	116.45 b±9.22	17.22 b±1.19	57.59 b±2.78	19.19 b±0.26
	PM-BC	4.32 a±0.07	169.37 b±9.15	0.71 a±0.04	27.80 a±1.64	5.50 a±0.10	215.69 a±7.90	12.02 c±1.20	47.24 c±5.59	15.75 c±1.86
	PMP-BC	4.48 a±0.23	181.28 a±4.47	0.73 a±0.06	29.86 a±2.10	5.60 a±0.08	226.91 a±10.73	10.24 c±0.80	41.64 c±5.63	13.88 c±1.88
Cd100	CK	3.55 b±0.14	41.34 c±2.11	0.30 c±0.04	3.46 c±0.35	3.03 b±0.08	35.30 c±2.47	61.27 a±1.72	71.41 a± 2.95	23.80 a±0.98
	WC-BC	3.59 b±0.05	62.52 b±4.92	0.32 c±0.02	5.65 b±0.54	3.21 b±0.19	55.86 b±4.32	37.67 b±3.02	65.39 b±1.92	21.79 b±0.64
	WCP-BC	3.64 b±0.09	66.65 b±2.22	0.37 b±0.03	6.76 b±0.76	3.17 b±0.14	58.04 b±4.37	32.13 c±2.94	58.68 c±2.54	19.56 c±0.85
	PM-BC	4.21 a±0.13	89.20 a±5.75	0.65 a±0.01	13.76 a±0.86	5.43 a±0.08	114.96 a±6.14	21.91 d±2.26	46.25 d±2.31	15.42 d±0.77
	PMP-BC	4.09 a±0.15	93.74 a±6.80	0.63 a±0.01	14.44 a±0.95	5.23 a±0.04	120.10 a±5.59	18.79 d±2.36	42.83 d±1.92	14.28 d±0.64
Cd1000	CK	2.20b±0.19	10.86 c±1.28	0.23 c±0.03	1.14 c±0.21	1.73 d±0.05	8.62 c±1.8	109.86 a±5.63	55.23 a±7.85	18.41 a±2.62
	WC-BC	2.37ab±0.10	15.10 b±2.12	0.26 bc±0.05	1.72 bc±0.58	1.69 d±0.03	10.82 bc±1.71	82.65 b±7.97	52.42 ab±5.56	17.47 ab±1.85
	WCP-BC	2.48a±0.05	17.16 b±1.55	0.30 b±0.04	2.07 b±0.32	1.95 c±0.03	13.51 b±1.38	75.40 b±8.76	50.72 abc±8.97	16.91 abc±2.99
	PM-BC	2.50a±0.11	21.67 a±1.14	0.44 a±0.03	3.79 a±0.57	3.11 a±0.02	27.03 a±2.59	46.26 c±2.97	40.32 bc±5.58	13.44 bc±1.86
	PMP-BC	2.44a±0.12	22.83 a±0.77	0.41 a±0.03	3.88 a±0.10	3.03 b±0.02	28.36 a±1.86	42.38 c±3.25	39.49 c±1.44	13.16 c±0.48

Each value is the mean of three replicates ± the standard deviation. The different lowercase letters in every Cd level mean significant differences between treatments based on the Duncan's Multiple Range test at $p \leq 0.05$

CONCLUSION

The use of biochar as a soil amendment to enable carbon sequestration has generated a lot of interest. But according to the findings here, biochars may have significant effects on cadmium behavior in the contaminated soil by altering its solubility, availability, and transport. This study clearly showed that wood chips- and poultry manure- derived biochars wheather in their raw or in phosphate-treated form, has the ability to remediate the Cd-contaminated soil in situ by immobilizing cadmium and reducing its availability to plants. Additionally, the studied types of biochar enhanced some soil properties, plant growth and nutrients uptake. Poultry manure-derived biochar was more effective in remediation of the Cd-contaminated soil and aqueous solutions than wood chips-derived biochar. Thus, it is possible to improve the phytostabilization of Cd-contaminated soils and the remediation of Cd-polluted water by using biochar derived from poultry manure. The P-treated wood chips- and poultry manure-biochar were more efficient in that remediation than their raw form especially in WC biochar case. Therefore, the phosphorus modification gave the biochars higher efficiency in Cd immobilization through precipitating it in non-soluble cadmium phosphate precipitate. Our study also, displayed that the P-treated biochar serve as P fertilizer to enhance plant growth and P availability in the amended soils. Further studied are needed for assessing the integration between biochar application and other soil remediation techniques such as phytoremediation for the best sustainable reclamation of heavy metals-contaminated soils.

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الفحم الحيوي والفحم الحيوي المحمل بالفوسفور المشتق من رقائق الخشب أو روث الدواجن قلل صلاحية وامتصاص الكادميوم بالنباتات من التربة الملوثة بالكادميوم

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الملخص

بحثت هذه الدراسة تأثير الفحم الحيوي (BC) والفحم الحيوي المحمل بالفوسفور (P-BC) المشتق من رقائق الخشب وروث الدواجن على تيسر الكادميوم للنبات في التربة الملوثة بالكادميوم. تم تفحيم رقائق الخشب وروث الدواجن بالحرارة عند 400 درجة مئوية لإنتاج الفحم الحيوي ، تمت معاملة الفحم الناتج بمحلول فوسفات البوتاسيوم ثنائى الهيدروجين لإنتاج الفحم الحيوي المحمل بالفوسفور (P-BC). تم تقييم كفاءة الفحم الحيوي والفحم الحيوى المحمل بالفوسفور في إزالة أيونات الكادميوم من المحاليل المائية المحتوية على 1 و10 و25 و50 و100 مجم كادميوم لتر$^{-1}$ وتم وصف ادمصاص الكادميوم باستخدام نماذج فرندلش ولانجمير وتيمكن كما أجريت تجربة أصص لتقييم تأثيرات انواع الفحم تحت الدراسة على نمو وامتصاص العناصر الغذائية وتيسر الفسفور والكادميوم لنباتات القمح في التربة الملوثة بتركيزات 1 و 10 و 100 و 1000 مجم كادميوم كجم$^{-1}$ تربة .تم اضافة انواع الفحم الحيوى المستخدمة الى التربة الملوثة بمستوى 3٪ (وزن: وزن) .أظهرت نتائج تجربة الادمصاص أن نموذج فرندلش يناسب ادمصاص الكادميوم ($R^2 = 0.9962 - 0.9988$) من المحاليل المائية أكثر من نماذج الأيزوثيرم الأخرى .أدت اضافة الفحم الحيوى المحمل بالفوسفور إلى زيادة الفسفور الميسر في التربة ونمو النبات وامتصاص النيتروجين والفسفور والبوتاسيوم .وفي الوقت نفسه، انخفضت تركيزات الكادميوم الميسر في التربة والنبات وامتصاصه مقارنة بالغير محمل والكنترول. و أعطى فحم روث الدواجن كفاءة أفضل من فحم الخشب في تحسين هذه الصفات .إضافة الفحم الحيوي المحضر من روث الدواجن المحمل بالفوسفور أو الغير محمل الى التربة الملوثة بالكادميوم يقدم أداة واعدة لتثبيت الكادميوم مع تأثيرات إيجابية على خصائص التربة ونمو النبات ، أيضا يمكن استخدام هذا الفحم الحيوي لإزالة الكادميوم من المياه الملوثة.