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Research Article

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Investigation of Adsorption Mechanisms in Competitive and Non-Competitive Systems: Cadmium Immobilization in Contaminated Calcareous Soil Amended with Bone-Derived Biochar

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Abstract

Biochar (BC) has emerged as a promising amendment to reduce the bioavailability and toxicity of heavy metals like cadmium (Cd) in contaminated soils. This study focuses on cow bone-derived biochar (CBBC), produced via pyrolysis at 550°C and further activated with $ZnCl_2$ (A-CBBC), to assess its effectiveness in immobilizing Cd in calcareous soils. The research includes comprehensive characterization of CBBC and raw bone powder (BP) using elemental analysis, XRF, BET, SEM, and FTIR. Cd mobility was evaluated through fractionation and adsorption isotherms under both competitive and non-competitive conditions. Results showed a 10% reduction in the accessible Cd fraction and mobility factor (MF) in soils treated with 5–7% CBBC after six months. Adsorption isotherms revealed that soluble Cd concentrations were twice as high in competitive systems compared to non-competitive ones. Cd levels in untreated soil were 2.7 times higher than in CBBC- and BP-treated soils. CBBC and BP enhanced Cd adsorption by 300 and 140 μmol kg^{-1}, respectively, compared to control. These findings highlight the potential of CBBC and BP to reduce Cd mobility in calcareous soils through cation exchange and surface complexation, offering a sustainable strategy for remediating heavy metal-contaminated alkaline soils.

Keywords: Bone Biochar; Heavy Metals; Soil Amendment; Cd Mobility, Cd Adsorption, Adsorption Mechanisms

1. Introduction

In recent years, there has been an increasing focus on the use of BC as a strategy to reduce the bioavailability of heavy metals in contaminated soils, particularly, the immobilization of Cd, which is a great concern due to its toxic effects on the environment and human health. The plant roots can access to Cd and incorporate it to the food chain. BCs can adsorb and retain heavy metals from aqueous solutions and limit their mobility in soil. BC has various structural and chemical properties that enhance its ability to adsorb heavy metals. These properties include a high specific surface area, a porous structure, and the presence of functional groups capable of binding heavy metals (Ghosh et al. 2021). Finding the dominant mechanism(s) is crucial for optimizing its application in contaminated sites. Transforming BP into BBC enhances its capacity to adsorb heavy metals (Foroutan et al. 2021). BBC is characterized by macropores with carbon, minerals and P_2O_5. These properties make BBC an effective soil amendment (Azeem et al. 2021). Bone-derived biochar (BBC), obtained from waste BP by pyrolysis process, can decrease the bioavailability of Cd through cation exchange capacity (CEC) mechanism and precipitation in aqueous solutions. The most effective mechanisms for immobilizing heavy metals by BBC in aqueous solutions is cation exchange of heavy metals with Ca^{2+} ions and surface protons. The weak bond between Ca^{2+} and carbonate (CO_3^{-2}) is broken in slightly acidic solutions, creating numerous vacant sites for the substitution of divalent cations (Martines et al. 2017). The exchange sites on the BBC surface can adsorb Cd in aqueous solutions that contain other divalent metal cations (Mendoza-Castillo et al. 2015). In the study by Rojas-Mayorga et al (2016), the amount of Cd substitution for calcium was greater than that for Ni and Zn, which was also approved by their X-ray photoelectron spectroscopy (XPS) results.

The increase in the specific surface area (SSA) of BBC may indirectly enhance its CEC and Cd adsorption capabilities. The transformation of macropores into meso- and micropores can increase the efficacy of this adsorbent in immobilizing heavy metals (Cisneros-Ontiveros et al. 2022). The pyrolysis process, influenced by the type of feedstock, results in an increase in the SSA and pore volume of the BC while causing a decrease in average pore size. This structural plays a crucial role in the physical immobilization of contaminants. Previous studies reported that BBC produced at pyrolysis temperatures between 500 to 900°C shows no significant differences in SSA, pore volume, or average pore diameter (Li et al. 2023). However, Biswas et al (2023) reported that Cd adsorption in aqueous solutions through ion exchange mechanisms is higher on the surface of BBC pyrolyzed at lower temperatures than those subjected to higher pyrolysis temperatures. This difference was attributed to the elevated levels of carbonate, pre-leached Ca^{2+} sites, external phosphorus, and the CO_3^{-2} /PO_4^{-3}.

Functional groups existing on the surface of BBC also play a pivotal role in its reactivity with pollutants in both aqueous and soil environments. The presence of hydroxyl, phosphate, and carboxyl groups enhances the BBC's immobilization capacity and promotes the formation of surface complexes. Specifically, carboxylic groups and aromatic structures adsorb metal cations by forming these surface complexes, while amine groups and aliphatic structures precipitate metals onto the BBC surface (Azeem et al. 2022).

In the soil ambient, the competition of heavy metals for exchange sites can enhance their mobility and increase the possibility of plant roots accessing them. Since, in soil solutions, cations are adsorbed on mineral surfaces with varying affinities. Among these, some cations, such as Pb and Zn, exhibit a greater affinity for binding to exchange sites compared to Cd (Ni et al. 2019; Davari et al. 2015). Accordingly, it is vital to implement soil remediation techniques that can effectively immobilize Cd, which is hazardous even at low concentrations.

Moreover, the high alkalinity of BBC can increase the pH of acidic soils (Amin et al. 2023) and consequently, reduce the activity and bioavailability of heavy metals for plant roots (Mei et al. 2022). At higher pH values, these metals precipitate on the surface of secondary soil minerals. In calcareous soils, on the contrary, BBC does not have a significant influence in the pH, as weak acidic groups and deprotonated organic anions make a strong pH buffer (Lu et al. 2022). Calcareous soils demonstrate greater capacity than acidic soils to immobilize heavy metals, due in part to precipitation and in part to the contribution of surface adsorption. Therefore, identifying the distinction between these two mechanisms is important. However, limited research has focused on the adsorption of Cd in the presence of BBC, particularly in calcareous soils. This research gap underscores the necessity to investigate the interactions between BBC and Cd and to provide more details on soil behaviour and Cd immobilization under real soil conditions. In this study, i) cow bone was used as the raw bone powder (BP) to produce cow bone BC through pyrolysis (CBBC) and a combination of pyrolysis and activation (A-CBBC). ii) All of mentioned substrates were characterized by instrumental analysis methods. iii) The CBBC were evaluated as agents for limiting Cd mobility by fractionation experiment in contaminated calcareous soil. And finally, iv) the quantity of Cd adsorbed by soil treated with CBBC, A-CBBC and BP in the non-competitive and competitive system were measured, and the potential mechanisms involved in this process were estimated.

2. Material and Methods

2.1 Study site and initial soil properties

A soil sample was collected from the surface layer (0-30 cm) around the zinc-lead mine at the Sormak area, Hamedan province, western Iran (48° 59′ 44″ E and 34° 10′ 20″ N). The physical and chemical properties of studied soil were measured by standard soil science methods; pH and electrical conductivity (EC) were measured using a pH meter (Metrohm, 827 pH lab, Switzerland) and an EC meter (912 Conductometer, Switzerland); organic carbon content (OC) by Walkley-black method, and CEC was determined by the Bawer method, in which sodium (Na) ion in a 1M sodium acetate salt at pH 8.2 is used as exchanging cation, and ammonium (NH_4) ion in an ammonium acetate salt at pH 7 is used as displacing cation. Na is detected by flame photometry (Jenway- PFP 7) (Rowell et al. 1994). Texture was evaluated by hydrometer methods (Bauycos 1962); equivalent calcium carbonate ($CaCO_3$) percentage was determined by reverse titration (Sims 1996), and heavy metals concentration by atomic absorption spectroscopy (Spectra AA-220 Varian) (Sposito et al. 1982).

2.2 Preparation of BBC

Cow bone wastes were obtained from local butcheries and thoroughly cleaned, then air dried for 1 week. A part of it was grounded and passed through a 0.5 mm sieve as BP; another part was placed in the pyrolysis reactor BBC under N_2 flow for 3 hours (temperature gradient +3°C/min) up to a final temperature of 550°C. The reactor was then switched off and cooled down to ambient temperature. Then, CBBC was grounded and passed through a 0.5 mm sieve. CBBC was activated

(A-CBBC) by 0.5 M zinc chloride salt (ratio of 1:12.5 w/V) at 80ºC for 24 hours (Angin et al. 2013).

2.2.1 BBC characterization

For characterization of bone products (BP, CBBC and A-CBBC), a 1:10 solid/water ratio was used to measure pH. Their CEC was measured by the Gaskin et al (2007) method. The composition was determined and quantified by X-ray fluorescence spectroscopy (PHILIPS instrument PW1410 model) and CHNS analyser (GmbH-Vario model). The textural and morphological properties were characterized by surface area analysis instrument (Brunauer, Emmett & Teller, BET, in a BELSORP MINI II model), heating under vacuum up to 450 °C, with t-plot, BET, Langmuir and Barrett, Joyner & Halenda (BJH) methods and scanning electron microscopy (SEM, JEOL JSM-840A), Functional groups were determined by Fourier Transform Infrared Spectroscopy, FTIR (TA Company, Q600 model) with argon and O_2 gases.

2.2.2 Soil Cd fractionation and MF experiment

To evaluate the soil Cd fractionation in the presence of CBBC, 200 g of air-dried soil, previously passed through a 2 mm sieve, were mixed with 0, 3, 5, and 7% (w/w) amounts of CBBC and left for 180 days in the incubator (at around field capacity (FC) moisture content, temperature at 25°C). After 1, 90, and 180 days, samples (2 g) were taken from each container and after oven drying (105°C for 24 hours), they were prepared for the fractionation experiment. For this purpose, the sequential extraction method (Sposito et al. 1982) was used. 0.5 M potassium nitrate (KNO_3) was added to samples (1:12.5 w/V) for soluble and exchangeable Cd fraction (f1); then, 0.5 M sodium hydroxide (NaOH) was added in the same ratio for organic Cd fraction (f2); then ethylene di-amine tetra acetic acid disodium (Na_2-EDTA) 0.05 M was used (same ratio) for the inorganic Cd fraction (f3), and 4 M nitric acid (HNO_3) (same ratio) for the residual Cd in the soil structure (f4). The supernatants of each fraction were analysed for Cd concentrations by atomic absorption spectrophotometer (SpectrAA 220). The percentage of mobility factor (MF) was measured by dividing f1 by the sum of all fractions and then multiplied by 100 for 180-day samples.

2.2.3 Cd adsorption isotherms

To determine adsorption isotherms, 0% and 2.5% (w/w) of BP, CBBC, and A-CBBC were added to air-dried soil samples (2 mm sieve) and kept under constant incubation conditions (at around field capacity (FC) moisture content, temperature at 25°C) for one month. Then, 3 g of oven-dried (105°C for 24 hours) soil from each sample was mixed with 25 ml of 0.01 M $CaCl_2$ as a background electrolyte solution in 50 ml tubes. For competitive conditions, various concentrations of $CdCl_2$, $PbCl_2$, $NiCl_2$, and $CuCl_2$ (0 to 680 μM) were added to mixture (spiked-Cd soil). While, for non-competitive conditions, only $CdCl_2$ (0 to 680 μM) was added. The suspensions were equilibrated for 20 h on a vertical end-over-end shaker in a constant temperature room (25 ± 2 °C). The suspensions were then centrifuged and filtered through the Whatman No. 42 filter paper (Davari et al. 2015). The supernatants were analysed for Cd concentrations by atomic absorption spectrophotometer (SpectrAA 220). The amount of adsorbed Cd (Q) was obtained from the difference in the concentration of initial Cd and equilibrium Cd (Ce). Adsorption data were fitted by linear and Freundlich equations (Eq. 1 and Eq. 2, respectively).

Equation 1: $Q = K_d \cdot C + b$

Equation 2: $Q= K_f \cdot C^n$

Where C is the equilibrium concentration of Cd ($\mu M\ L^{-1}$), Q is the amount of adsorbed Cd ($\mu M\ kg^{-1}$), and K_d is the adsorption coefficient of Cd or the slope of the equation ($1\ kg^{-1}$). b is intercept of the equation. K_f is the Freundlich adsorption coefficient ($1\ kg^{-1}$), and n is related to the adsorption intensity.

2.2.4 Statistics analysis

Statistical Analysis

Data visualization was conducted using Microsoft Excel (Microsoft Corp., Redmond, WA) and Sigma Plot version 14.0 (Systat Software, San Jose, CA). To evaluate treatment effects and their interactions, a completely randomized split-plot design was implemented, with CBBC treatment assigned as the main-plot factor and incubation time as the sub-plot factor. This design accommodates the hierarchical structure of the experiment, permitting separate estimation of error terms for main-plot and sub-plot factors. Statistical analysis was performed using SAS version 9.4 (SAS Institute, Cary, NC). A general linear model (GLM) procedure and adjusted-Tukey was applied to partition variation attributable to main-plot, sub-plot, and their interaction effects.

3. Results and Discussion

3.1 Soil chemical and physical properties

The results of soil physical and chemical properties are shown in Table 1. The soil sample exhibited a clay loam texture and an alkaline pH (7.54).

Table 1. Chemical and physical properties of the studied soil sample.

Physiochemical								
Texture	**Clay**	**Silt (%)**	**Sand (%)**	**$CaCO_3$ (%)**	**OC* (%)**	**pH**	**EC** (ds m^{-1})**	**CEC*** (cmol$_c$ kg^{-1})**
Clay loam	33.2	36	30.8	25	0.96	7.54	0.52	19.10
Elements (mmol kg-1)								
	Fe	**Mn**	**Zn**	**Cu**	**Ni**	**Pb**	**Cd**	
	918.5	34	4.86	1.12	1.99	2.68	0.01	

*Organic Carbon; ** Electrical Conductivity; ***Cation Exchange Capacity.

The EC and OC content in the soil sample were measured at 0.52 ds m^{-1} and 0.96%, respectively. Based on the amount of equivalent $CaCO_3$, the studied soil was calcareous. Considering the threshold limit for heavy metals (like Cd) in soils (MEF 2007), the concentration of heavy metals in our study soil suggests that it may be regarded as a contaminated site.

3.2 BBC characteristics

Table 2 presents data on the measured pH of bone products. The pH values for BP, CBBC, and A-CBBC were 9.8, 8.7, and 10.9, respectively.

Table 2. The X-ray fluorescence analysis and CHNS in bone products*.

Physiochemical properties	BP	CBBC	A-CBBC
pH	9.8	8.7	10.9
CEC (cmolc kg-1)	37	24	12
XRF (%)			
Fe_2O_3	0.45	0.44	0.45
CaO	30.08	36.18	17.96
Na_2O	0.95	1.01	2.80
MgO	0.48	0.79	0.08
K_2O	0.28	0.36	0.01
TiO_2	0.01	0.01	0.01
MnO	0.01	0.01	0.01
P_2O_5	26.38	34.51	22.46
LOI	41.00	26.15	29.34
Cl	n.d	n.d	3.50
Zn	n.d	n.d	23.0
CHNS (%)			
C	21.54	17.45	17.11
H	31.15	1.40	1.51
N	6.74	3.91	3.70
S	0.46	0.22	0.22
H/C	0.14	0.07	0.08

*Bone powder (BP); cow bone-derived biochar (CBBC); activated-CBBC(A-CBBC).

These results are consistent with previous studies and align with the average pH measurements observed for BBC (Azeem et al. 2022). The pyrolysis conditions had a significant effect on the chars' pH, as reported by Sun et al (2017), who found an increasing trend of pH with pyrolysis temperature.

The CEC value in BP, CBBC and A-CBBC samples were measured at 37, 24, and 12 cmolc kg^{-1}, respectively (Table 2). Park et al (2021) reported that pyrolysis temperature has a direct correlation with CEC. Their study presented CEC value for BBC produced at different temperatures, with a reported range of 13 to 30 cmolc kg^{-1}.

3.2.1 BBC composition

In terms of XRF analysis, as presented in Table 2, high levels of CaO and P_2O_5 were observed in all the samples, especially in the CBBC. In addition, concentrations of Zn (23.0%) and Cl (3.50%) were detected in the A-CBBC sample. because of CBBC activation by $ZnCl_2$, a high amount of Zn, and Cl appeared in A-CBBC.

The results of CHNS analysis indicate that BP have higher contents of carbon (C) (21.54%), hydrogen (H) (31.15%), nitrogen (N) (6.74%), and sulphur (S) (0.46%) compared to CBBC sample, with 17.45, 1.4, 3.91 and 0.07%, respectively. Although the C content of BP is higher than that of CBBC, but C content in CBBC might be more active (Park et al. 2013). Moreover, the H/C ratios for CBBC (0.07) and BP (0.14) were measured, indicating the degree of carbonization. Chun et al (2004) reported that during pyrolysis, the C content increases, while the levels of O_2 and H decrease. This leads to a reduced H/C ratio, indicating significant carbonization and a highly aromatic structure in the CBBC.

During pyrolysis, the concentrations of P_2O_5 (34.51%) and CaO (36.18%) increased in CBBC compare than BP. This reduction transforms structural Ca and P into their oxide forms due to the breakdown of the bone structure. The high levels of P_2O_5 and CaO in bone products, particularly in BBC sample, are attributed to the biological hydroxyapatite structure of bone (Iriarte-Velasco et al. 2016). The reduction in the amounts of P_2O_5 (22.46%) and CaO (17.96%) in A-CBBC is associated to the replacement of PO_4^{2-} by Cl^- and Ca^{2+} by Zn^{2+}. Additionally, high pyrolysis temperatures have been related to lower C and H contents in char samples (Qian et al. 2016).

3.2.2 BBC Textural properties

Textural properties, namely specific surface area (SSA), mass volume (Vm), total pore volume (TPV), and average pore diameter (APD) of bone products were estimated using the BET, Langmuir, T, and BJH equations (Table 3).

Table 3. Textural characteristics of bone products*.

Equations	**Bone products**	**Parameters**			
		SSA^{I} (m^2 g^{-1})	**V_m^{II} (cm^3 g^{-1})**	**TPV^{III} (cm^3 g^{-1})**	**APD^{IV} (ηm)**
BET	BP	0.71	0.16	0.002	13
	CBBC	48.0	11.0	0.171	14
	A-CBBC	25.0	5.70	0.170	27
Langmuir	BP	1.12	0.25	-	-
	CBBC	57.0	13.0	-	-
	A-CBBC	33.0	7.50	-	-
T	BP	0.34	-	-	-
	CBBC	32.0	-	-	-
	A-CBBC	19.0	-	-	-
BJH	BP	1.41	-	0.002	-
	CBBC	65.0	-	0.181	-
	A-CBBC	31.0	-	0.170	-

*Bone powder (BP); cow bone-derived biochar (CBBC); activated-CBBC (A-CBBC); specific surface area (SSA)^{I}, mass volume (Vm)^{II}, total pore volume (TPV)^{III} and average pore diameter (APD)^{IV}.

BP showed significantly lower amount of SSA, Vm, and TPV compared to CBBC and A-CBBC. The SSA amount fitted by the BJH equation for CBBC was 65 m^2 g^{-1}, which represented a significant increase compared to BP (1.41 m^2 g^{-1}). The amounts of V_m fitted by the Langmuir equation and TPV fitted by the BET equation were also 13 cm^3 g^{-1} and 0.17 cm^3 g^{-1} in CBBC, which were 52 and 85 times greater than BP, respectively. SSA, Vm, and TPV were measured for A-CBBC lower than CBBC. The APD amount was obtained 27 ɳm for A-CBBC, which was about twice that of CBBC. There was no difference between the APD measured of CBBC and BP.

The high SSA values typically indicate enhanced performance for pollutant adsorption. Iriarte-Velasco et al (2016) reported an SSA of 76.2 m^2/g for pork-derived biochar obtained by pyrolysis at 450°C using the BET equation. Rojas-Mayorga et al (2016) showed SSA and TPV values of 85 m^2/g and 0.22 cm^3/g, respectively, for CBBC at an average temperature of 825°C.

3.3 BBC Morphology

As seen in Figure 1, the surface of the BP is rough and irregularly ridged, with minimal visible pores, indicating a continuous and dense structure.

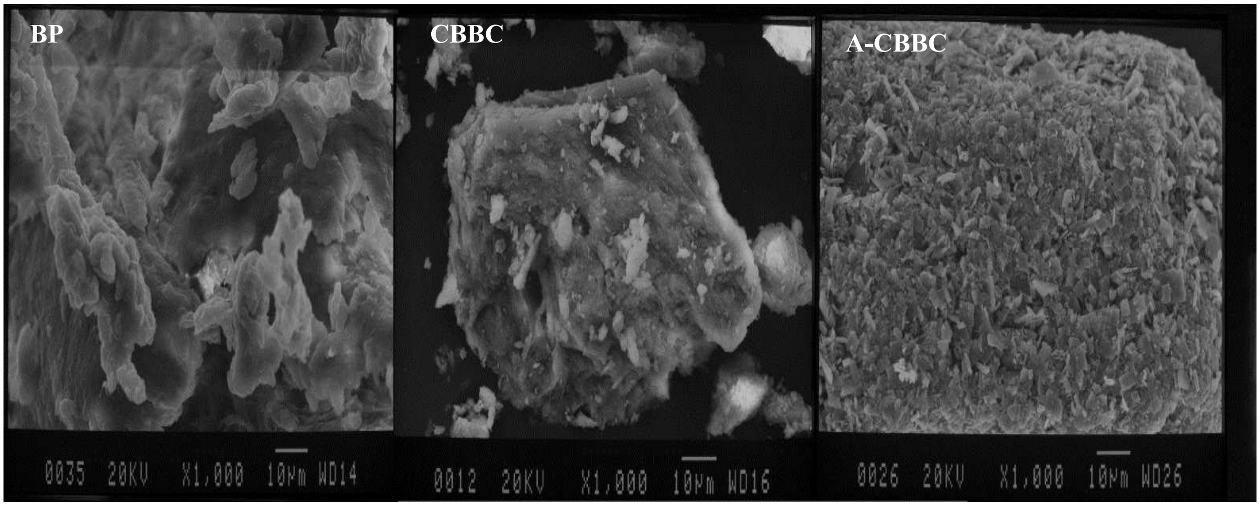

Figure 1. SEM micrograph of the bone powder (BP), bone biochar (CBBC) and activated- bone biochar (A-CBBC).

The pore volume increased relatively with bone charring, but there was no obvious difference between BP and CBBC samples. In sample A-CBBC, the surface completely covered with $ZnCl_2$, resulting in a multi-layered structure and the formation of new pores.

3.4 FT-IR analysis

Figure 2 illustrates the FT-IR spectra of BP, CBBC, and A-CBBC samples, respectively.

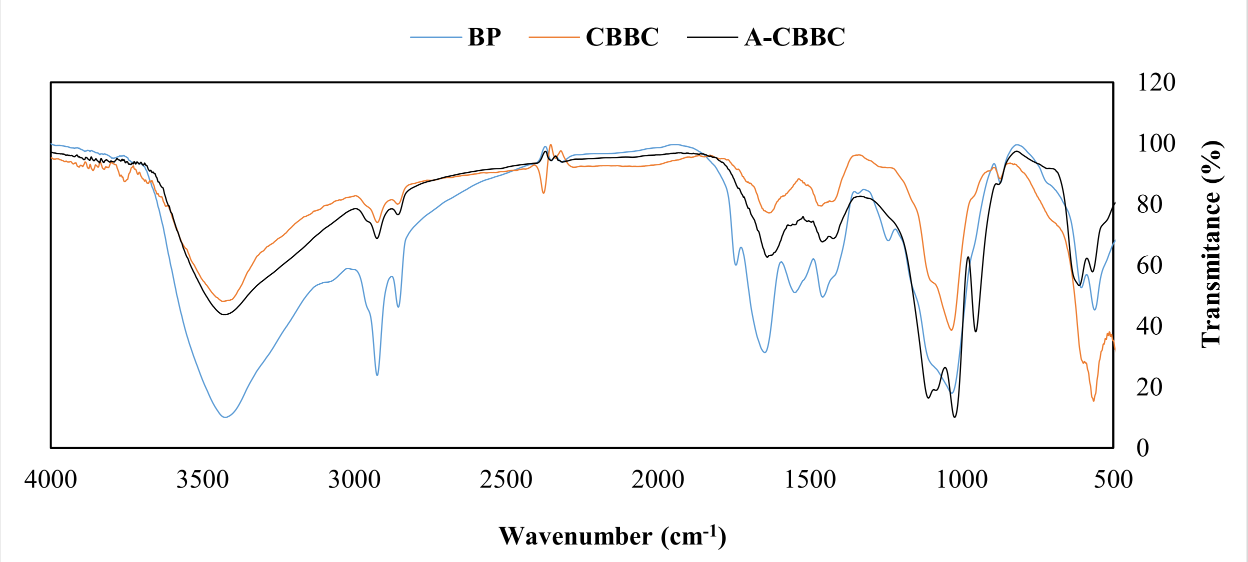

Figure 2. FT-IR spectrum for bone powder (BP), cow bone-derived biochar (CBBC) and activated-CBBC(A-CBBC) samples.

The peak observed at 3420 cm^{-1} is attributed to the strong stretching vibration of O-H groups in all samples and the peak at 2930 cm^{-1}, which corresponds to the asymmetric and symmetric stretching vibrations of –CH of the methylene group (Jung et al. 2019). Notably, the intensity of peaks corresponding to OH and CH groups decreased in the CBBC and A-CBBC samples, which subjected to high pyrolysis temperatures. The peak at 1540 cm^{-1} is attributed to the stretching vibration of the C=O band, indicating the presence of carbon in the structure of all samples. However, this peak was more pronounced in the BP sample. The peaks observed at 1415, and 1450 cm^{-1} indicated the symmetric vibration of the C-O bond in CO_3^{-2}, and the peak at 1635 cm^{-1} is attributed to the C=C vibration in aromatic hydrocarbons (Aboulkas et al. 2017). Furthermore, the peaks appearing at 567, 603 and 1037 cm^{-1} indicated the bending vibration of P–O of PO_4^{-3} (Zhang et al. 2019). The dominant functional groups in BP and BBC are C=O, C-O, C=C, P-O and O-H, which play an important role in the sorption of pollutants (Yang et al. 2020).

According to Xiao et al (2020) the presence of O- donor functional groups in BC adsorb heavy metals on the surface-by-surface complexing. Additionally, Cui et al (2016) reported that oxygenated functional groups enhance the sorption capacity of heavy metals by BCs through the exchange of ligands between hydroxyl adsorption sites and metal species.

3.5 Cd fractionation and MF

Figure 3 shows the results of Cd fractionation in the soil. In the 0% sample, the concentration of Cd in fraction f1 increased at 90 and 180 days of incubation, representing more than 20% of the total Cd in the soil.

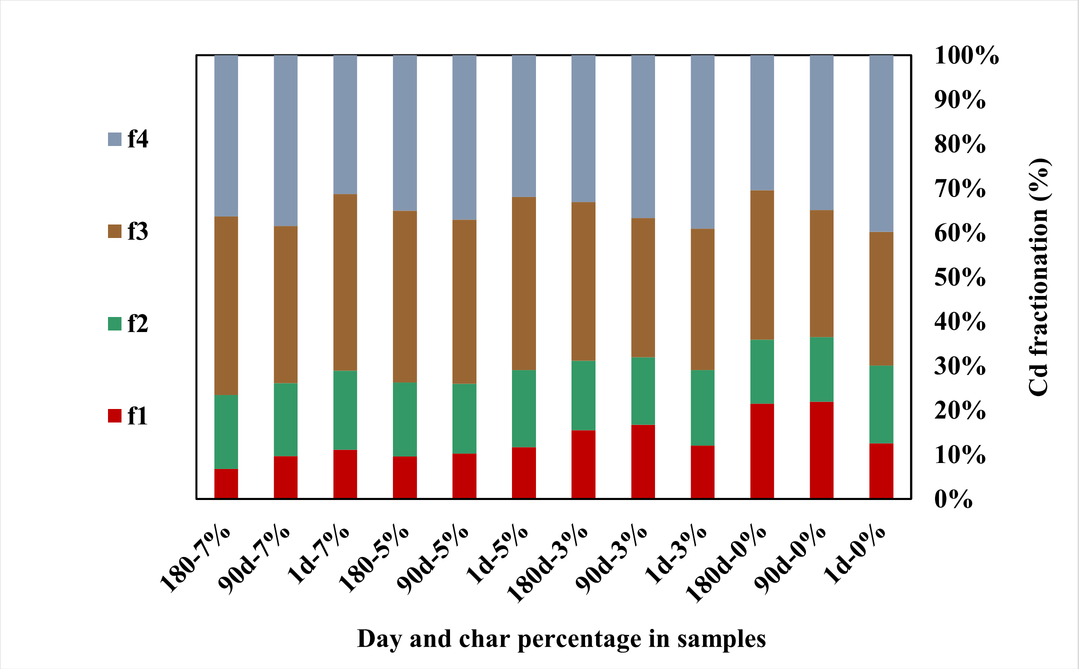

Figure 3. Cadmium (Cd) fractionation in soil treated with cow bone-derived biochar (CBBC).

Whereas, in the 5% and 7% samples, the concentration of Cd in f1 decreased to less than 10% of the total soil Cd during the incubation period. The concentration of Cd in other fractions (f2 and f3) did not show significant changes in the length of incubation and different CBBC levels.

Notably, the Cd concentration in fraction f4 increased at the end of the incubation period for the 7% CBBC sample. Additionally, the MF for Cd in the 0% sample was approximately 20% at the end of the incubation; however, with increased CBBC level, this index decreased to around 10% for the 7% CBBC sample. Our finding from the Cd fractionation experiment, conducted over an incubation period of 6 months, clearly showed that Cd immobilization increased in CBBC-treated soil. The results confirm the stability of CBBC. However, there was no distinction between soluble and exchangeable Cd in the f1 fraction.

According to the MF value, Cd exhibits significant mobility within the studied soil, posing a potential risk to environmental health and food safety. Even minimal concentrations exceeding 8 µmol/kg may enter the food chain through rhizosphere interactions and groundwater transport. The CBBC treatment, which effectively reduced the Cd mobility factor by 10%, presents a viable strategy for mitigating Cd mobility in soils stressed by this metal. Additionally, the use of BBC has demonstrated potential for Cd immobilization via adsorption mechanisms. This approach is particularly effective in calcareous soils, where smaller quantities of adsorbents are required compared to acidic soils due to the inherent buffering properties of the calcareous matrix and the tendency of heavy metals to precipitate within this pH range (Ming et al. 2016).

Soil moisture plays a critical role in the release and translocation of Cd. A continuous moisture regime leads to its mobilization from less accessible fractions to soluble and exchangeable forms (Dong et al. 2024). In the experimental setup, maintaining moisture around the FC point during the 180-day incubation period in the control soil resulted in a higher release rate compared to treated soils. These findings suggest that soil moisture regulation is crucial for controlling Cd bioavailability and mitigating potential contamination risks.

Additionally, the statistical results regarding the interaction between incubation time and CBBC treatment levels on Cd fractionation are presented in Table 4.

Table 4. Interaction effect of CBBC and incubation time on changes in each Cd fraction in soil.

Time	**CBBC levels**	**F1**	**F2**	**F3**	**F4**
(day)	(%)	(μM kg^{-1})			
180	7	8.45^{a}	20.55^{a}	49.81^{ab}	45.01^{a}
180	5	11.92^{a}	20.73^{a}	48.22^{ab}	43.59^{a}
90	7	11.92^{a}	20.37^{a}	47.77^{ab}	47.77^{a}
90	5	13.34^{ab}	20.64^{a}	48.75^{ab}	48.75^{a}
1	7	14.23^{abc}	22.95^{a}	51.15^{b}	40.21^{a}
1	5	14.95^{abc}	22.15^{a}	50.00^{ab}	40.83^{a}
1	3	15.30^{abc}	21.62^{a}	40.65^{ab}	49.82^{a}
1	0	15.57^{abc}	21.71^{a}	37.36^{a}	49.37^{a}
180	3	20.64^{bc}	20.91^{a}	47.77^{ab}	44.21^{a}
90	3	22.06^{c}	20.10^{a}	41.46^{ab}	48.48^{a}
180	0	30.60^{d}	20.55^{a}	47.95^{ab}	43.32^{a}
90	0	30.78^{d}	20.37^{a}	40.12^{ab}	49.01^{a}

Similar letters indicate non-significance in the column.

In f1, which is the most significant fraction concerning the effect of CBBC on f1, a notable difference was observed between the 5% and 7% levels compared to 0% at 90 and 180 days. In the 7% treatment, after 90 and 180 days, the f1 amount was 11.92 and 8.45 µmol/kg of soil, respectively, while in the 0% treatment, it measured 30.78 and 30.60 µmol/kg of soil at the same times. The f1 level in the 5% treatment was 13.34 and 11.92 µmol/kg of soil after 90 and 180 days, respectively. No statistically significant differences were observed in f2, f3, and F4, although in f3, a difference between the 7% and 0% levels was noted on the first day of incubation, likely to indicate CBBC's effect on Cd binding to the carbonate component of the soil.

3.6 Cd adsorption isotherm

Cd adsorption experiment results were summarized in Figure 4.

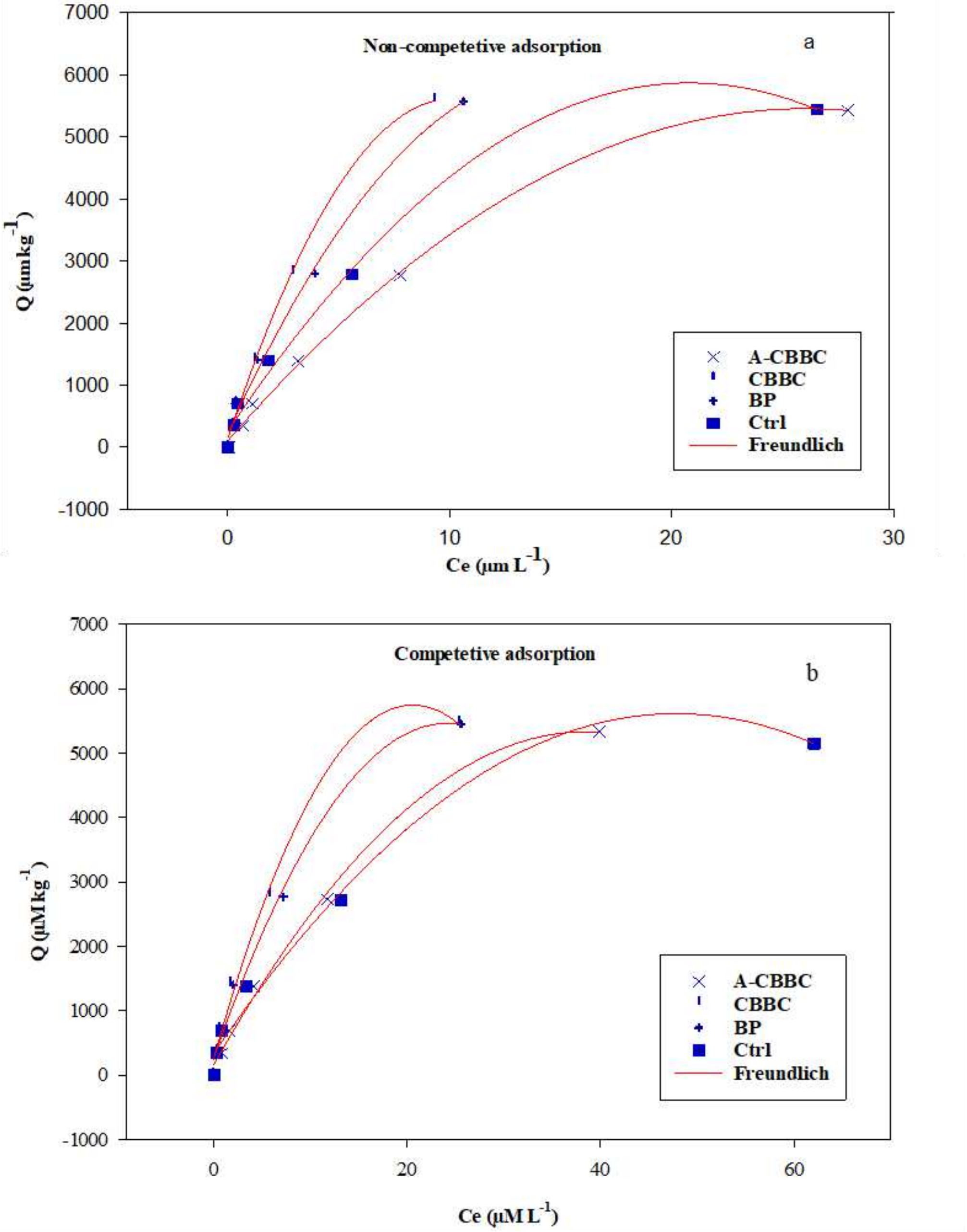

Figure 4. Cadmium (Cd) adsorption isotherm in soils treated with bone powder (BP), cow bone-derived biochar (CBBC), and activated-CBBC (A-CBBC) under competitive (a) and non-competitive conditions (b).

The findings indicate that the amount of Cd adsorbed (Q) increased under both non-competitive (Fig. 4a) and competitive (Fig. 4b) systems in soils treated with BP, CBBC and A-CBBC compared to the ctrl soil. As a result, the Cd concentration in the soil solution decreased by approximately 10 μM L^{-1}, while the Ce was 2.7 times higher in the ctrl soil. At low concentrations of spiked Cd, the amount of Q in treated and ctrl soils was not significantly different. As the initial concentration of Cd increased, the amount of Q exceeded 5000 in all treatments. At the highest spiked Cd concentration, the amount of Ce in the CBBC and BP treatments was 9.3 and 10.6 in non-competitive system and 25.4 and 25.6 in competitive system, respectively; meanwhile, in ctrl soil, the values were 27.9 in non-competitive system and 62 in competitive system. The amount of Ce for soil treated with A-CBBC in non-competitive system was not significantly different from that of the ctrl soil; however, its value decreased in competitive system to 39.8. The soil treated with CBBC and BP showed significantly higher Cd adsorption compared to the ctrl soil. Moreover, soil treated with CBBC and BP adsorbed more than 140 μM kg^{-1} of Cd under non-competitive system and more than 300 μM kg^{-1} of Cd under competitive system compared to ctrl soil.

In soils where multiple metals exceed permissible limits, competition for adsorption sites on soil minerals and adsorbents becomes increasingly relevant. Understanding the interaction between solution and solid phases, as well as adsorption mechanisms, is essential for optimizing soil remediation strategies. As illustrated in Figures 4a and 4b, Cd adsorption in control and treated soils aligns more closely with the experimental Freundlich adsorption equation than with a simple linear adsorption model. At lower Ce values, stronger adsorption is observed, while adsorption intensity gradually diminishes as Ce values increase.

Table 5 presents the indices derived from fitting experimental data to both linear adsorption equations (K_d) and the Freundlich model (K_f and n), alongside statistical indices (R^2 and SE). K_d and K_f serve as reliable estimates of the affinity of soil particles and adsorbents for Cd ions.

Table 5. Parameter values obtained from fitting linear and Freundlich equations to Cd adsorption isotherms under competitive and non-competitive conditions in soils treated with BP, CBBC, A-CBBC, and the control soil.

Treatment	**Experiment**	**Linear**			**Freundlich**			
		K_d I	**R^2 II**	**SE III**	**K_f I**	**n IV**	**R^2**	**SE**
Ctrl [1]	Competitive	75.15	0.89	214.48	2.82	1.92	0.99	0.80
	Non-competitive	188.01	0.90	210.12	2.96	1.74	0.97	1.07
BP [2]	Competitive	199.71	0.94	172.78	2.88	1.58	0.99	1.02
	Non-competitive	502.65	0.97	116.30	3.07	1.53	0.99	1.24
CBBC [3]	Competitive	198.33	0.91	206.36	2.93	1.62	0.98	1.06
	Non-competitive	576.30	0.96	140.78	3.08	1.40	0.99	1.27
A-CBBC [4]	Competitive	126.93	0.95	162.26	2.65	1.41	0.98	0.86
	Non-competitive	184.88	0.94	167.62	2.75	1.38	0.98	0.97

Control soil (ctrl)[1]; Bone powder (BP)[2]; cow bone-derived biochar (CBBC)[3]; activated-CBBC (A-CBBC)[4]; approximation of the soil and bone BBC particles affinity for Cd (K_d and K_f)[I], coefficient of determination (R^2)[II], standard error between experimental data and model prediction (SE)[III] and degree of heterogeneity in the sorption site (n)[IV].

Notably, K_d values were significantly higher in BP- and CBBC-treated soils than in ctrl or A-CBBC-treated soils, highlighting the superior Cd adsorption capability of BP and CBBC amendments. Furthermore, this coefficient varies between competitive and non-competitive systems, emphasizing the necessity of context-specific assessments for adsorption dynamics.

Lower K_d values correspond to increased Cd presence in solution, making it more susceptible to transport and plant uptake. In contrast, higher Kd values indicate greater metal retention by the adsorbent, enhancing Cd immobilization. K_d values further serve as critical estimates for comparing adsorption capacities across different treatments under identical experimental conditions. Increased K_d values in non-competitive systems, compared to competitive systems, suggest heightened toxicity risks in real-world scenarios where multiple metals coexist.

Higher R^2 values and lower SE values signify an improved model fit for the Freundlich adsorption equation.

The K_f coefficient represents the ratio of metal adsorption in the solution phase, indicating the general tendency of Cd to bind to soil and adsorbents. Alloway (1995) demonstrated that distribution coefficients provide valuable comparative metrics for assessing adsorption capacities across different soil matrices and adsorbent materials.

To simulate experimental conditions, an electrolyte solution (0.01 M $CaCl_2$) was equilibrated with calcite, a representative component of calcareous soils, with log Ksp = -8.48 and CO_2 partial pressure at 0.00038 atm. The solution parameters were adjusted to pH 7.54 and 25°C, and $CdCl_2$, $NiCl_2$, $CuCl_2$, and $PbCl_2$ were introduced to prevent precipitation at the selected initial concentrations. Simulation results indicated that in non-competitive and competitive systems, respectively, over 99% and 97% of the initial Cd concentration remained in the system as Cd ions. All species remained below the saturation limit, except for the $CdCO_3$ mineral (otavite), which exhibited log Ksp = -11.34 in the non-competitive system and log Ksp = -10.98 in the competitive system. Given these findings, precipitation effects on Cd retention are considered negligible under these experimental conditions, allowing a confident attribution of adsorption results to surface adsorption mechanisms.

In competitive systems, Cd adsorption dynamics are influenced by interactions with other metal ions. The presence of Zn in A-CBBC activated with $ZnCl_2$ likely leads to Zn occupying charged adsorption sites, intensifying competition between Cd and Zn. Similarly, the inclusion of additional cations in competitive systems results in antagonistic interactions, further diminishing Cd adsorption efficiency. These findings underscore the necessity of precise decision-making in contaminated site management.

The Cd adsorption isotherm experiments conducted on BP-, CBBC-, A-CBBC-treated soils, and the control soil demonstrate that the Freundlich model offers a superior fit compared to the linear adsorption equation. While empirical regression models facilitate the interpretation of adsorption data, alternative models such as Langmuir, two-site Langmuir, and BET exhibit lower alignment with experimental findings. This study highlights the complexity of Cd adsorption behaviour in competitive and non-competitive systems, reinforcing the need for tailored remediation strategies in contaminated environments.

BP and CBBC exhibited a high capacity for the adsorption of Cd from soil solutions, which could be due to the high CEC and the presence of P=O functional groups and complex formation on both adsorbent surfaces. BP exhibited a high Cd adsorption capacity and showed no significant difference compared to CBBC, although its SSA value was significantly higher than that of BP. The higher CEC of the BP sample accounts for the increased Cd adsorption by the surface-charged sites. In the case of A-CBBC activated by $ZnCl_2$, a significant proportion of the exchange sites were occupied by Zn, leading to the formation of PO_4-Zn surface complexes. Consequently, the CEC and the capacity for Cd immobilization were decreased, indicating that this activation method was ineffective in increasing Cd sorption by A-CBBC. In the case of Cd and Pb, the efficiency of this types of adsorbents is higher (Gruden et al. 2017; Azeem et al. 2022). Mei et al (2022) reported that the use of pork BBC in contaminated soils reduced the mobility of heavy metals, such as Cd in the soluble fraction after two months, and subsequently, in the plant tissue. They proposed several potential adsorption mechanisms: firstly, surface complexation; secondly, the exchange of cations, specifically Ca^{2+} with Cd^{2+}; thirdly, the precipitation of Cd with PO_4, Ca, and the hydroxyl groups of BBC; and finally, the indirect effect of BBC pH's on Cd precipitation.

The effective mechanisms reported to reduce Cd mobility in BC-treated soil for a long incubation period (300 days) were complexation with humus, precipitation, electrostatic interaction (CEC), and modification by microorganisms (He et al. 2024).

Biswas et al (2023) reported that the X-ray diffraction results showed the spatial distribution and adsorption of Cd ions on the surface of BBC hydroxyapatite mineral in aqueous solution in a 3D manner. The main adsorption mechanism was identified as ion exchange, while the amount of precipitation was found to be minor. Notably, the study found that more than 91% of the crystalline calcium ions were replaced by Cd ions.

Lei et al (2020) estimated that more than 74% of the Cd dissolved at pH 5.5 was adsorbed by cation exchange and surface complex formation and approximately 24% was precipitated. Although, as pH increases, precipitation can play a more significant role in the immobilization of Cd.

The solubility and availability of Cd in soil solutions are also dependent on pH. However, due to the inherent complexity and multiphase nature of soil, as well as its greater buffering capacity, especially in calcareous soils, compared to aqueous solutions, the contributions of these mechanisms are variable.

Calcareous soils show a high capacity to precipitate trace elements due to the presence of CO_3^- and HCO_3^- ions, thereby risk of these soils is lower than that of acidic soils (Rezaei et al. 2021). However, elements such as Cd at low concentrations pose a risk of entering the food chain and causing adverse health effects (Shi et al. 2022).

According to the results of the fractionation experiment, under a constant moisture regime, approximately 20% of the total Cd in the control soil migrated into the accessible fraction in the long term. Additionally, in the adsorption isotherm experiment under competitive conditions, the soluble Cd concentration in the control soil was approximately 60 μmol L^{-1}, underscoring the importance of adsorption mechanisms facilitated by amendment substances in treated soils.

4. Conclusion

In this study, bone-derived biochar (CBBC) was prepared at 550°C, with a portion activated using $ZnCl_2$. Characterization of CBBC, A-CBBC, and bone powder (BP) was conducted through instrumental analysis, revealing significant amounts of P_2O_5 and CaO, which increased post-charring. The textural properties of CBBC, measured by BET analysis, exhibited notable changes, particularly in the specific surface area (SSA), total pore volume (TPV), and average pore diameter (APD). FTIR analysis identified functional groups including -CH, P-O, C-O, C=O, and O-H, supporting the results of other characterizations. The addition of CBBC to contaminated soils resulted in a substantial reduction of bioavailable Cd and Cd mobility fraction (MF) over an extended incubation period. Isotherm adsorption experiments demonstrated that soils treated with BP and CBBC had a high capacity for Cd adsorption, significantly reducing soluble Cd levels compared to control soils. The competitive and non-competitive adsorption systems revealed that CBBC and BP effectively adsorbed Cd, with CBBC showing impressive adsorption capacity. However, the presence of Zn in A-CBBC occupied exchange sites, reducing its Cd sorption efficiency. Consequently, the Cd sorption mechanism of CBBC and BP in calcareous soils is likely dominated by cation exchange capacity (CEC). These findings highlight the potential of CBBC and BP as effective amendments for the remediation of heavy metal-contaminated soils, emphasizing the importance of biochar (BC) properties in optimizing soil health and reducing environmental contamination.

References

Aboulkas A, Hammani H, El Achaby M, Bilal E, Barakat A (2017) Valorization of algal waste via pyrolysis in a fixed-bed reactor: production and characterization of bio-oil and bio-char. Biores Technol 243:400–408. https://doi.org/10.1016/j.biortech.2017.06.098

Alloway BJ (1995) Heavy metals in soils. Blackie Academic and Professional, London, p 368

Amin EEAZ (2023) Effect of co-applying different nitrogen fertilizers with bone char on enhancing phosphorus release in calcium carbonate-rich soil: an incubation study. JPNSS 23:1565–1575. https://doi.org/10.1007/s42729-023-01217-3

Angın D, Altintig E, Köse TE (2013) Influence of process parameters on the surface and chemical properties of activated carbon obtained from biochar by chemical activation. Biores Technol 148:542–549. https://doi.org/10.1016/j.biortech.2013.08.164

Azeem M, Ali A, Jeyasundar PGSA, Li Y, Abdelrahman H, Latif A, Ronghua L, Basta N, Li G, Shaheen SM, Rinklebe J, Zhang Z (2021) Bone-derived biochar improved soil quality and reduced Cd and Zn phytoavailability in a multi-metal contaminated mining soil. Environ Pollut 277:116800. https://doi.org/10.1016/j.envpol.2021.116800

Azeem M, Shaheen SM, Ali A, Jeyasundar PGSA, Latif A, Abdelrahman H, Li R, Almazroui M, Niazi MNK, Sarmah AK, Li G, Rinklebe J, Zhu Y-G, Zhang Z (2022) Removal of potentially toxic elements from contaminated soil and water using bone char compared to plant- and bone-derived biochars: a review. J Hazard Mater 427:128131. https://doi.org/10.1016/j.jhazmat.2021.128131

Bauycos GJ (1962) Hydrometer methods improved for making particle size of soils. Agron J 56:464–465

Biswas PP, Rathod J, Chiang CY, Liang B, Wang CC, Lee YC, Wang SL (2023) First principal observation documenting the three-dimensional uptake of cadmium and spatial distribution of cadmium hydroxyapatite mineral in bone char. Chemosphere 337:139357. https://doi.org/10.1016/j.chemosphere.2023.139357

Chun Y, Sheng G, Chiou CT, Xing B (2004) Compositions and sorptive properties of crop residue-derived chars. Environ Sci Technol 38:4649–4655. https://doi.org/10.1021/es035034w

Cisneros-Ontiveros HG, Medellín-Castillo NA, Aldama-Aguilera C, Ilizaliturri-Hernández CA, Cruz-Briano SA, Labrada-Delgado GJ, Flores-Rojas AI (2022) Optimization of synthesis variables and characterization of devilfish bone chars for the removal of cadmium (II) from water. MRS Adv 7:997–1003. https://doi.org/10.1557/s43580-022-00456-3

Cui X, Hao H, Zhang C, He Z, Yang X (2016) Capacity and mechanisms of ammonium and cadmium sorption on different wetland-plant derived biochars. Sci Total Environ 539:566–575. https://doi.org/10.1016/j.scitotenv.2015.09.022

Davari M, Rahnemaie R, Homaee M (2015) Competitive adsorption-desorption reactions of two hazardous heavy metals in contaminated soils. Environ Sci Pollut Res 22:13024–13032. https://doi.org/10.1007/s11356-015-4505-8

Dong Q, Xiao C, Cheng W, Yu H, Liu G, Liu Y, Jiang G (2024) Phytoavailability, translocation, and accompanying isotopic fractionation of cadmium in soil and rice plants in paddy fields. J Hazard Mater 477:135321. https://doi.org/10.1016/j.jhazmat.2024.135321

Foroutan R, Peighambardoust SJ, Hosseini SS, Akbari A, Ramavandi B (2021) Hydroxyapatite biomaterial production from chicken (femur and beak) and fishbone waste through a chemical-less method for Cd^{2+} removal from shipbuilding wastewater. J Hazard Mater 413:125428. https://doi.org/10.1016/j.jhazmat.2021.125428

Gaskin JW, Speir A, Morris LM, Ogden L, Harris K, Lee D, Das KC (2007) Potential for pyrolysis char to affect soil moisture and nutrient status of a loamy sand soil. http://hdl.handle.net/1853/48168

Ghosh D, Maiti SK (2021) Biochar assisted phytoremediation and biomass disposal in heavy metal contaminated mine soils: a review. Int J Phytoremediation 23:559–576. https://doi.org/10.1080/15226514.2020.1840510

Government Decree on the Assessment of Soil Contamination and Remediation Needs. Ministry of the Environment, Finland (2007). Accessed June 2024. https://www.finlex.fi/en/laki/kaannokset/2007/en20070214.pdf

Gruden E, Bukovec P, Zupančič M (2017) Preliminary evaluation of animal bone char as potential metal stabilization agent in metal contaminated soil. Acta Chim Slov 64:3. https://doi.org/10.17344/acsi.2016.2889

He Y, Mi B, Luo C, Zhao W, Zhu Y, Long C, Wu F (2024) Mechanisms insights into Cd passivation in soil by lignin biochar: transition from flooding to natural air-drying. J Hazard Mater 134565. https://doi.org/10.1016/j.jhazmat.2024.134565

Iriarte-Velasco U, Sierra I, Zudaire L, Ayastuy JL (2016) Preparation of a porous biochar from the acid activation of pork bones. Food Bioprod Process 98:341–353. https://doi.org/10.1016/j.fbp.2016.03.003

Jung KW, Lee SY, Choi JW, Lee YJ (2019) A facile one-pot hydrothermal synthesis of hydroxyapatite/biochar nanocomposites: adsorption behavior and mechanisms for the removal of copper (II) from aqueous media. Chem Eng J 369:529–541. https://doi.org/10.1016/j.cej.2019.03.102

Lei S, Zhu L, Xue C, Hong C, Wang J, Che L, Qiu Y (2020) Mechanistic insights and multiple characterizations of cadmium binding to animal-derived biochar. Environ Pollut 258:113675. https://doi.org/10.1016/j.envpol.2019.113675

Li Y, Liu J, Han L, Wei B, Liu X (2023) Influence of pyrolysis atmosphere, temperature, and particle size co-regulation on the physicochemical properties of bone char. J Environ Chem Eng 11:111357. https://doi.org/10.1016/j.jece.2023.111357

Lu HL, Li KW, Nkoh JN, He X, Hong ZN, Xu RK (2022) Effects of the increases in soil pH and pH buffering capacity induced by crop residue biochars on available Cd contents in acidic paddy soils. Chemosphere 301:134674. https://doi.org/10.1016/j.chemosphere.2022.134674

Martins JI, Órfão JJM, Soares OSGP (2017) Sorption of copper, nickel and cadmium on bone char. Prot Met Phys Chem Surf 53:618–627. https://doi.org/10.1134/S2070205117040153

Mei H, Huang W, Wang Y, Xu T, Zhao L, Zhang D, Pan X (2022) One stone two birds: Bone char as a cost-effective material for stabilizing multiple heavy metals in soil and promoting crop growth. Sci Total Environ 840:156163. https://doi.org/10.1016/j.scitotenv.2022.156163

Mendoza-Castillo DI, Bonilla-Petriciolet A, Jáuregui-Rincón J (2015) On the importance of surface chemistry and composition of bone char for the sorption of heavy metals from aqueous solution. Desalin Water Treat 54:1651–1662. https://doi.org/10.1080/19443994.2014.888684

Ming H, Naidu R, Sarkar B, Lamb DT, Liu Y, Megharaj M, Sparks D (2016) Competitive sorption of cadmium and zinc in contrasting soils. Geoderma 268:60–68. https://doi.org/10.1016/j.geoderma.2016.01.021

Ni BJ, Huang QS, Wang C, Ni TY, Sun J, Wei W (2019) Competitive adsorption of heavy metals in aqueous solution onto biochar derived from anaerobically digested sludge. Chemosphere 219:351–357. https://doi.org/10.1016/j.chemosphere.2018.12.053

Park JH, Choppala G, Lee SJ, Bolan N, Chung JW, Edraki M (2013) Comparative sorption of Pb and Cd by biochars and its implication for metal immobilization in soils. Water Air Soil Pollut 224:1–12. https://doi.org/10.1007/s11270-013-1711-1

Park JH, Yun JJ, Kang SW, Kim SH, Cho JS, Wang JJ, Seo DC (2021) Removal of potentially toxic metal by biochar derived from rendered solid residue with high content of protein and bone tissue. Ecotoxicol Environ Saf 208:111690. https://doi.org/10.1016/j.ecoenv.2020.111690

Qian L, Zhang W, Yan J, Han L, Gao W, Liu R, Chen M (2016) Effective removal of heavy metal by biochar colloids under different pyrolysis temperatures. Bioresour Technol 206:217–224. https://doi.org/10.1016/j.biortech.2016.01.065

Rezaei MJ, Farahbakhsh M, Shahbazi K, Marzi M (2021) Study of cadmium distribution coefficient in acidic and calcareous soils of Iran: Comparison between low and high concentrations. Environ Technol Innov 22:101516. https://doi.org/10.1016/j.eti.2021.101516

Rojas-Mayorga CK, Mendoza-Castillo DI, Bonilla-Petriciolet A, Silvestre-Albero J (2016) Tailoring the adsorption behavior of bone char for heavy metal removal from aqueous solution. Adsorpt Sci Technol 34:368–387. https://doi.org/10.1177/0263617416658891

Rowell DI (1994) Soil science method and application. Longman Group, London

Shi J, Du P, Luo H, Wu H, Zhang Y, Chen J, Gao H (2022) Soil contamination with cadmium and potential risk around various mines in China during 2000–2020. J Environ Manag 310:114509. https://doi.org/10.1016/j.jenvman.2022.114509

Sims JT (1996) Lime requirement. In: Sparks D (ed) Methods of soil analysis. Part 3. Chemical methods. SSSA Book Series No. 5. Soil Science Society of America and American Society of Agronomy, Madison, pp 491–515. https://doi.org/10.2136/sssabookser5.3.c17

Sposito G, Lund LJ, Chang AC (1982) Trace metal chemistry in arid-zone field soils amended with sewage sludge: I. Fractionation of Ni, Cu, Zn, Cd, and Pb in solid phases. Soil Sci Soc Am J 46:115–121. https://doi.org/10.2136/sssaj1982.03615995004600020009x

Sun J, He F, Pan Y, Zhang Z (2017) Effects of pyrolysis temperature and residence time on physicochemical properties of different biochar types. Acta Agric Scand B Soil Plant Sci 67:12–22. https://doi.org/10.1080/09064710.2016.1214745

Xiao J, Hu R, Chen G (2020) Micro-nano-engineered nitrogenous bone biochar developed with a ball-milling technique for high-efficiency removal of aquatic Cd(II), Cu(II) and Pb(II). J Hazard Mater 387:121980. https://doi.org/10.1016/j.jhazmat.2019.121980

Yang Y, Sun C, Lin B, Huang Q (2020) Surface modified and activated waste bone char for rapid and efficient VOCs adsorption. Chemosphere 256:127054. https://doi.org/10.1016/j.chemosphere.2020.127054

Zhang Q, Wang J, Lyu H, Zhao Q, Jiang L, Liu L (2019) Ball-milled biochar for galaxolide removal: Sorption performance and governing mechanisms. Sci Total Environ 659:1537–1545. https://doi.org/10.1016/j.scitotenv.2019.01.005

Statements and Declarations

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Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request. Due to the nature of the data (e.g., large file sizes, proprietary software formats, or institutional restrictions), they are not publicly available. However, all relevant data used in the analysis and interpretation are described within the article and its supplementary materials.

Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Conflict of interest

There is no conflict of interest in this paper.

Authors' Contributions

All authors contributed to the study conception and design. Methodology, investigation, software use, data collection and analysis were performed by Sobhan Mohammadi and Abolfazl Khademi-Jolgehnezhad. The first draft of the manuscript was written by Sobhan Mohammadi and all authors commented on previous versions of the manuscript. Subsequent versions of the manuscript were prepared by all authors, who as well have read and approved the final manuscript. Supervision, revision and funding acquisition was done by Ghasem Rahimi, María Gonzalez Alriols and M. Mirari Antxustegi.

Ethical Approval

Not applicable

Consent to Participate

Not aplicable

Consent to Publish

Not aplicable