

Article

Ball Mill, Humic Acid, and Rock Phosphate-Modified Conocarpus Biochar for Efficient Removal of Heavy Metals from Contaminated Water

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Abstract: An increasing trend of anthropogenic activities such as urbanization and industrialization has resulted in induction and accumulation of various kinds of heavy metals in the environment, which ultimately has disturbed the biogeochemical balance. Therefore, the present study was conducted to probe the efficiency of conocarpus (*Conocarpus erectus* L.) waste-derived biochar and its modified derivatives for the removal of lead (Pb), cadmium (Cd), copper (Cu), and zinc (Zn) from aqueous solutions. Biochar was produced at 600 °C and modified with humic acid (1:10 *w/v* ratio) and rock phosphate (0.5:1 *w/w* ratio). Additionally, produced biochar, as well as humic acid and rock phosphate-modified biochars, were subjected to ball milling separately. Equilibrium and kinetics batch experiments were conducted to investigate heavy metals adsorption on synthesized adsorbents. Adsorption isotherms and kinetics models were employed to explore the adsorption efficiency of produced materials for metals adsorption. Among all the applied adsorbents, ball-milled biochars showed comparatively higher adsorption compared to un-milled biochars. Humic acid and rock phosphate-modified milled biochar showed the highest adsorption capacity for Pb (18.85 mg g⁻¹), while rock phosphate-modified milled biochar showed the highest adsorption capacity for Cu and Zn (24.02 mg g⁻¹ and 187.14 mg g⁻¹), and humic acid modified biochar adsorbed maximum Cd (30.89 mg g⁻¹). Adsorption isotherm study confirmed Freundlich as the best-suited model ($R^2 = 0.99$), while kinetics adsorption was well described by the pseudo-second-order ($R^2 = 0.99$). Hence, it was concluded that ball-milled biochar modified with humic acid and rock phosphate could potentially remove heavy metals from contaminated water.

Keywords: biochar modification; ball milling; anthropogenic activities; conocarpus; remediation



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1. Introduction

Hysterical anthropogenic activities, such as industrial waste discharge, mining activities, fossil fuel extraction and refining, and agriculture waste, invasively release heavy metals into terrestrial and aquatic ecosystems, which ultimately disturbs their natural biogeochemical balance [1]. In their natural balance, such kinds of heavy metals do not pose any serious contamination risks, but with continuous and excessive release into the environment, they cause serious environmental pollution, disturb fauna and flora, and pose serious health threats to human beings due to their non-degradable, persistent, and toxic nature [2]. Among these heavy metals, lead (Pb) ranks second after arsenic (As) in the list of hazardous heavy metals due to its potentially toxic nature and global manifestation [3]. Fossil fuel combustion (85 Gg/year), metals extraction (25 Gg/year), and waste released by agricultural activities (0.9 Gg/year) are the main source of Pb discharge in terrestrial

and aqueous environments [4,5]. The increasing rate of Pb accumulation in the natural environment severely affects the terrestrial ecosystem, pollutes water bodies, threatens plant growth and microbial activity, and presents a particular health risk to human beings, including reduced educational performance in children and curtailed social skills and physical activities among adults [6]. In addition to Pb, cadmium (Cd), which is generally released from mining activities and domestic wastes, also poses serious human health risks, including kidney damage and bone fracture [7]. On the other hand, copper (Cu) and zinc (Zn) mainly pollute soil and water resources through fertilizer application, waste disposal, and metal-contaminated municipal and industrial waste and deteriorate environmental quality and public health [8].

It is very important to find and apply sustainable and effective remediation technologies to restore and rehabilitate large-scale contaminated soil damaged by heavy metals toxicity. It includes a number of physical, chemical, and biological techniques to systematically clean and restore or potentially reduce hazardous effects of metals contamination. Metals stabilization and their soil immobilization, employing chelating agents, solvent extraction, thermally assisted soil treatment, and adsorption by a number of applied soil amendments are commonly applied techniques to overcome heavy metals (Cr, Cu, Pb, Cd, As, Zn) based soil contamination [9]. Most of these techniques are costly, utilize costly chemicals and excessive salts, and generate secondary pollution, while adsorption is a widely accepted remediation technique since it is a feasible, cost-effective, and easy-to-practice technique [10]. Among a number of adsorbents used in the adsorption process, biochar has attained ample attention globally due to its excellent adsorptive characteristics and economic feasibility [11].

Biochar, a solid by-product produced by thermal degradation of organic wastes under a limited supply of oxygen [12], has shown great potential in mitigating abiotic stress such as soil salinity, metal toxicity, and drought stress in soil and plants [13]. Biochar is an organic material possessed with excellent adsorptive characteristics, such as porous surface structure, plenty of surface functional groups, high surface area and cation exchange capacity, and plentiful residual carbon fraction [14]. Earlier and recent studies endorsed the application of biochar as eco-friendly material in mitigating metal and other organic pollutant toxicity [15]. Nzediegwu et al. [16] found that adsorption capacity of wheat straw-derived biochar for Pb from wastewater was 165 mg g^{-1} . Park et al. [7] found 93.5% and 88.4% removal of Pb and Cd, respectively, from aqueous solution by using chicken manure-derived biochar. In an adsorption study, Chen et al. [17] reported ample adsorption capacity of pomelo peel-derived biochar (81.91 mg g^{-1}) for Cu.

Recently, pre- and post-pyrolysis fabrication of biochar with foreign materials and its combination with various solvent and organic materials (biochar composite) has gained great attention, since such kinds of surface and chemical modifications improve biochar's efficiency as a soil amendment, further refining its adsorption capacity for organic and inorganic pollutants in solid and aqueous phase and enhancing crop productivity. Madhavi et al. [18] reported an increase in soil cation exchange capacity (CEC) and maize crop production upon the integrated application of biochar combined with humic acid and NPK. Zhang et al. [19] found a significant increase in (48.9% and 55%) removal of Cd and Pb by application of humic acid and rock phosphate-activated biochar. In another research work, Liu et al. [20] found 76% and 87.2% removal of Pb and Cd through the integrated application of humic acid-activated dolomite rock phosphate with biochar. Additionally, rock phosphate-activated biochar showed three folds more stabilization (68–74%) and lower uptake of Pb as compared to only biochar application (25–30%) [19]. Liu et al. [21] found a five times higher adsorption of Cu by humic acid-impregnated biochar compared to pristine biochar.

Ball milling has been endorsed as a cost-effective and practically feasible method that reduces solid material particle size to nanoscale by mechanical action [22], which is a very helpful tool for generating novel and fabricated nanoscale adsorbents [23]. Enhanced surface porosity, an increased number of microscopic pores, and the high external specific

surface area of ball-milled biochar make it a more suitable and efficient adsorbent for various kinds of pollutants. In his research work, Xiao et al. [24] found a comprehensive increase in Pb sorption (558.8 mg g^{-1}) with cow bone meal-derived ball-milled biochar, which was 64.61% higher than un-milled biochar. Ion exchange and precipitation were classified as adsorption mechanisms by Cao et al. [25] for Pb adsorption by wheat straw derived ball-milled biochar for excellent adsorption of Pb (134 mg g^{-1}), which was three folds less in pristine biochar (46.33 mg g^{-1}). Lyu et al. [26] investigated how ball milling affected the physicochemical and sorptive characteristics of biochar. Their findings demonstrated that the increased external and internal surface areas of the ball mill-biochar exposed its graphitic structure, which improved Ni adsorption via strong cation-p interaction. Additionally, by way of surface complexation and electrostatic interaction, the rise in acidic surface functional groups promoted Ni adsorption by ball milled-biochar. Ball milling, therefore, has a great deal of promise to boost the effectiveness of eco-friendly biochar for a variety of environmental applications. To the best of our knowledge, the combined effects of ball milling, humic acid, and rock phosphate-modified biochar on heavy metals removal have not been investigated previously. Therefore, the prime goals of this study were focused on the production of conocarpus (*Conocarpus erectus* L.) based biochar, its modification with humic acid and rock phosphate to activate surface functional groups and optimize pH, and the generation of their ultrafine and nanoscale variants by ball milling. These produced (un-milled) and fabricated (milled) biochars were employed to remove Cd, Cu, Zn, and Pb from aqueous solutions and to investigate their adsorption capacity for metal adsorption in the aqueous phase.

2. Materials and Methods

2.1. Biochar Production and Modification

Conocarpus waste was used as feedstock to produce biochar. Feedstock was collected from the agriculture farm of King Saud University, Riyadh, Kingdom of Saudi Arabia. After collection, feedstock was washed with deionized water and cut into small pieces prior to pyrolysis. Biochar was prepared by using the modified procedure of Ahmad et al. [14]. Feedstock was pyrolyzed in a muffle furnace (Wisetherm FH14, Germany) at 600°C for 2 h at a $5^\circ\text{C}/\text{min}$ heating rate. After this, pyrolysis-produced biochar was collected, ground, sieved by 0.5 mm size mesh, stored in an airtight container, and labeled as BC. The prepared BC was used to synthesize composites using the modified method reported by Giwa et al. [27]. Briefly, BC was treated with humic acid (HA) at a 1:10 *w/v* ratio. Simply, 10 g BC was taken in a glass beaker, and 0.15 M HA was added using the aforementioned ratio. The mixture was put on a reciprocal shaker for 5 h at 140 rpm. Afterward, the suspension was filtered using Whatman 42 filter paper, solid material on the filter paper surface was collected and oven dried at 60°C , followed by crushing and sieving by a 0.5 mm size screen, stored in an airtight container, and labeled as HA-BC. Rock phosphate (RP) was ground to a very fine particle size of 0.20 mm before mixing with biochar. Freshly produced BC and RP powders were thoroughly mixed at a 1:0.5 *w/w* ratio, respectively, and the final product was tagged as RP-BC. Later, a similar RP was mixed with HA-treated BC at the above-mentioned weight ratio, and the final product was labeled as HARP-BC.

2.2. Ball Milling

All these produced and treated materials (BC, HA-BC, RP-BC, and HARP-BC) were subjected to ball milling separately to generate ultrafine biochars (BCs). Briefly, a specific amount of each produced and treated charred material was added to a ball mill (FRITSCH, Pulveritsette 7, Germany). The metal balls were used for the ball milling process. The ball milling was performed for 24 h at a regular cycle of 20 min milling and 10 min interval at 500 rpm. Additionally, BC and RP-BC were wet-ball-milled by adding deionized water at a 1:0.5 *w/v* ratio to produce finer-grade milled MBC and RP-MBC. Finally, all milled

biochar-based materials were collected, stored in a container, and labeled MBC, WMBC, HA-MBC, RP-WMBC, and HARP-MBC according to their composite types.

2.3. Biochar Characterization

All the produced, modified, and milled charred materials were analyzed for their physio-chemical and surface characteristics. All kinds of BCs were analyzed chemically by following standard procedures [28]. Electrical conductivity (EC) and pH were determined by EC (YSI Model 35) and pH (WTW-pH 523) meter from suspension of 1:10 *w/v* ratio. The CEC was measured following the Spark [29] method. The ASTM D1762-84 [30] method was followed to determine moisture contents, volatiles, ash contents, and residual carbon fractions in BCs. All materials were analyzed using scanning electron microscopy (SEM, EFI S50 Inspect, Netherlands) to investigate surface morphology, and an X-Ray diffractometer (MAXima X XRD-7000, Shimadzu, Japan) was employed to observe the mineralogical structure and crystallinity of biochars. Afterward, Fourier transformation infrared spectroscopy (Bruker Alpha-Eco ATR-FTIR, Bruker Optics, Inc.) analyses were conducted at a wavelength range of 600–4000 cm^{-1} to investigate the surface functional groups. Adsorbents were analyzed by Brunauer–Emmett–Teller (BET) to investigate the surface area of adsorbents.

2.4. Adsorption Experiment

2.4.1. Adsorption Isotherm

To investigate the adsorption capacity of BCs for Pb, Cd, Cu, and Zn, adsorption batch experiments were conducted. Analytical grade $\text{Pb}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$ were used as source compounds, and solutions of different concentrations of metals (0, 10, 25, 50, and 100 mg L^{-1}) were prepared separately. In total, 0.05 g of each type of BCs was added in a 50 mL solution of varying metals concentration in a plastic (polypropylene) tube, and the pH of the solution was adjusted to 5. Samples were placed on reciprocal shakers. After shaking for 24 h, the samples were removed and filtered using Whatman 42 filter paper. Filtrates were collected and analyzed using Inductively Coupled Plasma Optical Emission spectroscopy (PerkinElmer Optima 4300 DV ICP-OES) to estimate metal adsorption on BCs. Equation (1) was used to calculate adsorption [31].

$$q_e = \frac{(C_o - C_e) \times V}{m} \quad (1)$$

where, C_o describes the initial concentration of metal (mg L^{-1}), C_e is the equilibrium concentration of metal (mg L^{-1}), V is the volume of the metal solution (L), m is the mass of the adsorbent (g), and q_e is the adsorbed metal concentration (mg g^{-1}) at equilibrium. To further investigate the adsorption mechanism and adsorption parameters, widely accepted Langmuir, Freundlich, and Temkin models [32–34] were applied to experimental data using Equations (2) and (3).

$$q_e = \frac{Q_o b C_e}{1 + b C_e} \quad (2)$$

$$q_e = K_F C_e^{1/n} \quad (3)$$

$$q = \frac{RT}{b} \ln(AC_e) \quad (4)$$

where, C_e is the solution-phase equilibrium concentration (mg L^{-1}), q_e is the solid phase equilibrium concentration (mg kg^{-1}), Q_o is the Langmuir isotherm sorption capacity (mg g^{-1}), b is the enthalpy-related sorption constant (mg L^{-1}), n is the sorption intensity constant, and K_F is the Freundlich sorption capacity constant (g L^{-1}).

2.4.2. Kinetics Study

Kinetics experiments were conducted to observe the adsorption behavior of all produced and modified biochars at specific time intervals. Briefly, 0.05 g of each kind of BCs was added to the already prepared 25 mg L⁻¹ metals solution with a pH value adjusted to 5. Samples were placed in a shaker and were removed at regular time intervals (0, 30, 60, 120, 240, 480, 960, and 1440 min), filtered, and filtrates were analyzed by ICP-OES for Pb, Cd, Cu, and Zn concentration. Following (Equations (5)–(8)), kinetics models were applied to experimental data to observe metal adsorption on BCs [35].

$$\text{First order:} \quad \ln q_t = \ln q_0 - k_1 t \quad (5)$$

$$\text{Pseudo-second-order:} \quad \frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{q_e} t \quad (6)$$

$$\text{Power function:} \quad \ln q_t = \ln b + k_f (\ln t) \quad (7)$$

$$\text{Intraparticle diffusion:} \quad q_t = a + k_{id} t^{0.5} \quad (8)$$

where, q_t is the adsorbed quantity of metal (mg g⁻¹) by the sorbents after extraction at time t (min), and q_0 is the adsorbed quantity of metal at $t = 0$. The rate constants of the first-order and second-order adsorptions (mg g⁻¹ min⁻¹) are described by k_1 and k_2 , respectively. Additionally, k_{id} is the intraparticle diffusion rate (mg g⁻¹ min^{-0.5}), k_f is the rate coefficient value (mg g⁻¹ min⁻¹), a and b are constants.

2.5. Statistics

To analyze experimental data statistically, Statistics 8.1 software was used. The treatment effect was further interpreted and compared by LSD (least significance difference) at a 5% probability level [36].

3. Results and Discussion

3.1. Biochar Characterization

The pristine and modified BCs showed distinctive characteristic differences among them (Table 1). A higher pH (10.14) was noted for BC produced at 600 °C, which could be due to the release of acidic functional groups by thermal treatment [37]. HA-BC pH dropped nearly two-fold, which might be due to the addition of acidic ions in biochar by humic acid addition. Likewise, the pH of RP-BC and HARP-BC also dropped to 7.96 and 6.10, respectively, which might be due to the combined effects of the humic acid and rock phosphate addition to BC and loss of basic ions on rock phosphate addition [38]. A slight decrease in EC of HA-BC and RP-BC was noted in comparison to pristine biochar, while no significant differences were found in pH and EC of un-milled and milled BCs. Lower moisture contents were found in all kinds of produced, treated, and milled BCs except WMBC (4.38%), which could be due to the addition of water during the milling process. Consistently lower moisture contents and volatiles showed the effects of higher thermal treatment, while on the contrary, higher fractions of ash and residual carbon were found in all BCs. Higher ash contents indicated accumulation and conglomeration of mineral compounds in BCs, while a higher fraction of residual carbon showed more carbon stability and recalcitrant potential of BCs [39]. No significant differences in moisture content, mobile matter, ash, and fixed carbon content were found among un-milled and milled BCs. However, HARP-BC and WMBC showed slightly higher volatile matter along with a minor decrease in fixed carbon contents.

SEM analysis of tested adsorbents showed ample porosity and broad channel on the BC surface (Figure 1). The porous surface of BC indicated the release of tar and clogged substances in BC pores at a higher pyrolysis temperature [40]. Additionally, it could be due to the higher rate of degradation and decomposition of organic compounds and the release

of water molecules and other volatiles. In comparison to its original BC, a higher number of meso-pores were found in ball-milled BCs. The appearance of a greater number of surface pores could be due to the mechanical action of ball milling. Additionally, some micro-scale amorphous structures were found on the milled BC surface, which commonly appeared due to the mechanical effects of ball milling [41]. Further tubular pore structures, along with thin layers, were found in HA and RP derivatives of milled BC, which indicated the successful modification of pristine BC by HA and RP [10].

Table 1. Proximate and chemical analyses result of conocarpus biochar and its un-milled, milled, and modified derivatives.

Material	BC	HA-BC	HARP-BC	RP-BC	MBC	HA-MBC	HARP-MBC	WMBC	RP-WMBC
Moisture %	2.30 ± 0.15	2.04 ± 0.02	2.35 ± 0.072	2.04 ± 0.50	1.96 ± 0.01	2.03 ± 0.09	2.30 ± 0.05	4.38 ± 0.21	2.43 ± 0.019
Mobile matter %	16.03 ± 1.17	11.49 ± 2.46	18.81 ± 1.93	13.55 ± 2.1	12.90 ± 3.21	15.81 ± 1.97	15.43 ± 1.35	17.36 ± 2.15	16.09 ± 3.70
Ash %	20.86 ± 3.14	24.56 ± 3.25	17.87 ± 5.48	19.64 ± 2.6	21.3 ± 3.99	20.57 ± 3.93	21.21 ± 4.64	20.97 ± 1.92	24.62 ± 3.64
Resident matter %	60.81 ± 4.88	61.91 ± 3.94	60.97 ± 3.40	64.77 ± 2.48	63.81 ± 1.81	61.60 ± 4.09	61.06 ± 5.50	57.29 ± 3.06	56.86 ± 4.37
pH (1:10)	10.14 ± 0.07	5.13 ± 0.18	7.96 ± 0.02	6.10 ± 0.02	9.37 ± 0.13	5.96 ± 0.34	7.95 ± 0.07	6.03 ± 0.04	6.41 ± 0.06
EC [†] (dSm ^{−1})	0.56 ± 0.06	0.42 ± 0.04	0.36 ± 0.03	0.49 ± 0.03	0.62 ± 0.00	0.41 ± 0.064	0.49 ± 0.01	0.43 ± 0.015	0.59 ± 0.01

[†] Electrical conductivity, BC = Biochar, HA-BC = Humic acid modified biochar, RP-BC = Rock phosphate modified biochar, HARP-BC = Humic acid and rock phosphate modified biochar, MBC = Ball-milled biochar, HA-MBC = Humic acid modified ball-milled biochar, HARP-MBC = Humic acid and rock phosphate modified ball-milled biochar, WMBC = Ball-milled biochar with water, RP-WMBC = Rock phosphate modified ball-milled biochar with water.

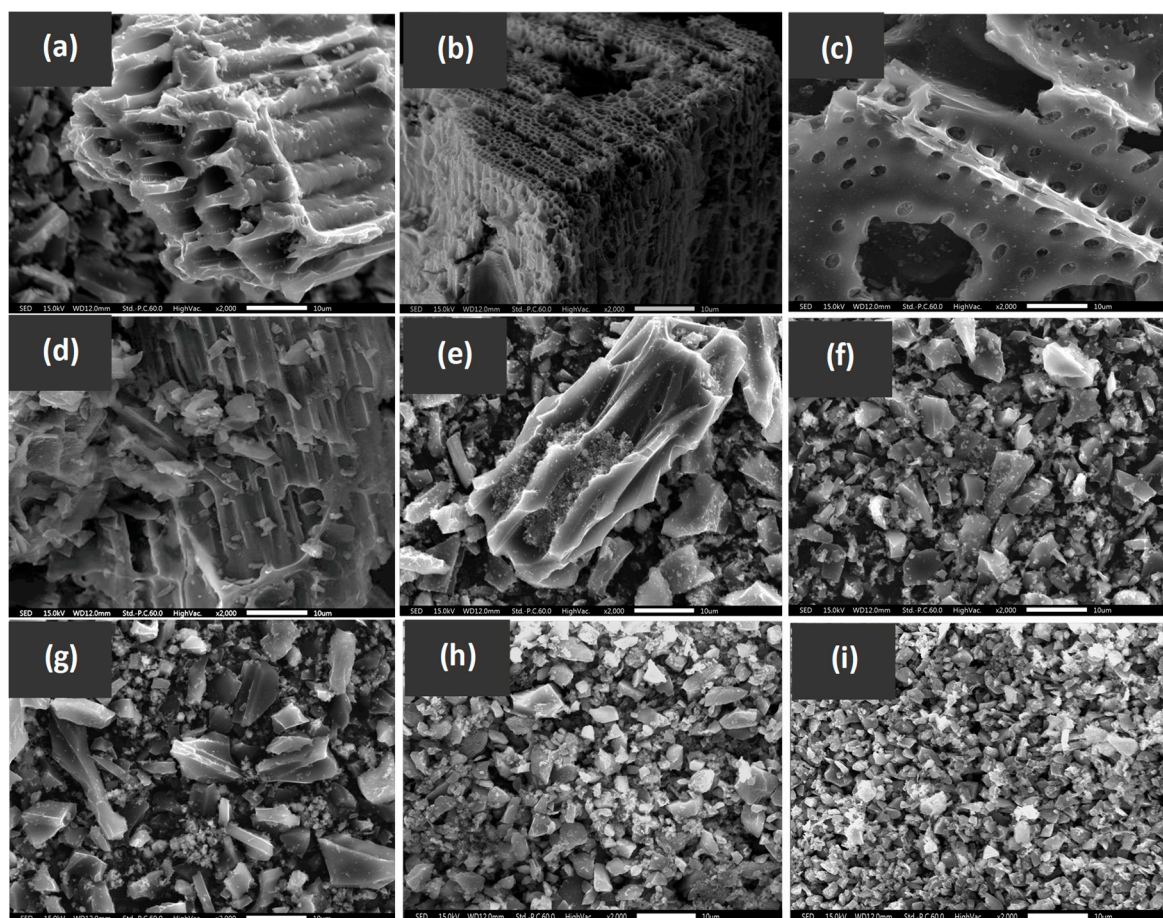


Figure 1. Scanning electron microscope images of conocarpus biochar and its un-milled, milled, and modified derivatives. (a) Biochar, (b) Humic acid-modified biochar, (c) Rock phosphate-modified biochar, (d) Humic acid and rock phosphate-modified biochar, (e) Ball-milled biochar, (f) Humic acid-modified-ball-milled biochar, (g) Humic acid and rock phosphate-modified ball-milled biochar, (h) Ball-milled biochar with water, (i) Rock phosphate-modified ball-milled biochar with water.

FTIR spectra of selected un-milled and milled BCs are described in Figure S1 (Supplementary Data). Broad bands in BCs in the range of 813–1761 cm^{-1} indicated the presence of C-H stretching [27]. These bands were sharper and moved slightly on the right side in milled derivatives of HA and RP-modified BC, which could be due to the chemical modification of BC with HA and RP and physical modification by ball milling. A similar trend of band shifting and enhanced intensity of oxygenated functional groups was found by Yuan et al. [42]. Additionally, small bands at 1222 cm^{-1} in HA-MBC and at 1219 cm^{-1} at RP-WMBC, 1290 cm^{-1} at BC, and 138 cm^{-1} at MBC indicated the presence of oxygenated carboxylic functional groups (C=O) along with epoxy carboxyl (C-O) and aromatic structures containing carbon fractions [21]. Moreover, small bands at 1729 cm^{-1} , 2146 cm^{-1} , 2167 cm^{-1} , and 2334 cm^{-1} attributed to oxygenated C=O groups; since oxygen is not completely removed from BCs. It also confirmed the presence of C=C bands, carbonized carboxylic functional groups, and protonated aromatic carbon rings due to BC acidification, especially in HA-MBC [43]. Additionally, more sharp and broad bands of carboxylic and hydroxyl groups in milled derivatives of selected BCs indicated more dispersion of these surface functional groups under the mechanical effect of ball milling. Small bands of phosphate groups appeared at 1740–2407 cm^{-1} , which were mainly due to RP composite with BC [44].

The mineral composition of the prepared BC is described in Figure S2. Small peaks of degraded organic compounds were found along with a moderate peak at 3.84 Å confirming the presence of quartz [45], while a broad peak was found in both un-milled and milled BC at 3.01 Å followed by the appearance of 2.78 Å, 2.48 Å, 2.28 Å, 2.08 Å, and 1.90 Å, which showed the presence of amorphous carbon fraction in carbon-enriched BCs [46] along with calcite (CaCO_3) and calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) minerals (hydroxyapatite) [24,44]. The varying intensity of these peaks in BCs showed the conversion of amorphous carbon fractions into more symmetrical crystalline fractions under the influence of the heat treatment of biomass. Similar peaks of a smaller size and lower intensity appeared and slightly shifted right in the milled BC, which indicated the degradation of the crystalline structure of carbon compounds under the effects of mechanical milling [24]. Broad peaks at 3.84 Å and 3.86 Å in HARP-BC and RP-WMBC mainly corresponded to phosphate compounds ($(\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O})$, $\text{Ca}_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$) due to the enrichment of BC with RP [47]. The presence of phosphate compounds was attributed to the reaction between P radicles and aromatic carbon compounds produced by pyrolysis, which confirmed the homogeneous distribution of P on charred material [48]. Klupfel et al. [49] and Uchimiya and Hiradate [50] also reported the generation of new P-C (phosphorus and carbon) compounds in manure-derived BC after their treatment with rock phosphate and phosphorus compounds. Concurrently, HA-modified BCs showed characteristic peaks of $\text{K}_2\text{CrO}_3 \cdot 1.5\text{H}_2\text{O}$ at 2.78–3.01 Å and a typical graphite carbonized compounds crystalline structure at 3.86 Å [51].

Table 2 represents BET analyzed surface area of the produced adsorbents. The highest surface area was found in HA-MBC, followed by RP-WMBC and MBC. The surface area was increased by 36–81.5% in the milled variant of pristine BC, which indicated integrated effects of HA addition and ball milling. Likewise, the pore volume increased, while the pore size decreased with ball milling. Overall, BC exhibited the lowest surface area (173.076 $\text{m}^2 \text{g}^{-1}$), followed by RP-BC (188.850 $\text{m}^2 \text{g}^{-1}$). Results showed that HA-modified biochar showed more increase in surface area as compared to RP-modified biochar. At the same time, a significant increase in surface area was noted in RP-WMBC, which again endorsed promising effects of ball milling on enhancing BC surface area. The higher surface area of milled variants of BC showed higher surface porosity which ultimately favored their adsorption capacity for metal ions. A similar trend of increasing surface area was found by Lyu et al. [26] while studying the effects of ball milling on the physicochemical and sorptive properties of BC.

Table 2. BET surface area of conocarpus biochar and its un-milled, milled, and modified derivatives.

Adsorbents	Surface Area ($\text{m}^2 \text{g}^{-1}$)	Pore Volume ($\text{cm}^3 \text{g}^{-1}$)	Pore Size ($\text{\AA}$)
BC	173.076 ± 8.793	0.1433	33.128
HA-BC	210.668 ± 6.786	0.2256	25.689
HARP-BC	207.993 ± 7.726	0.1337	25.717
RP-BC	188.850 ± 7.914	0.1462	36.908
MBC	234.99 ± 15.646	0.1724	29.350
HA-MBC	320.887 ± 7.902	0.1729	21.975
HARP-MBC	263.450 ± 8.315	0.1485	22.556
WMBC	241.671 ± 6.108	0.1380	22.851
RP-WMBC	272.645 ± 9.847	0.1760	25.826

BC = Biochar, MBC = Ball-milled biochar, HA-MBC = Humic acid-modified ball-milled biochar, RP-WMBC = Rock phosphate-modified ball-milled biochar with water.

3.2. Adsorption Experiments

3.2.1. Equilibrium Adsorption

Cadmium (Cd)

Equilibrium adsorption of Cd by un-milled (BC, HA-BC, HARP-BC, and RP-BC) and milled (MBC, HA-MBC, HARP-MBC, WMBC, and RP-WMBC) BCs were analyzed by employing different adsorption isotherm models including Langmuir, Freundlich, and Temkin. Among applied isotherm models, Langmuir and Freundlich were fitted well, indicating both mono and multilayer chemisorption [52]. A higher R^2 value (Table 3) of Langmuir model parameters using experimental data indicated homogeneous surface adsorption of Cd on adsorbents [53]. Figure S3a–f shows adsorption isotherm analyzed by Langmuir, Freundlich, and Temkin adsorption models. A higher Q_e (mg g^{-1}) value of HA-BC indicated the higher adsorption capacity of HA-BC, which was equally high in HARP-BC and RP-BC, and the lowest adsorption was found in pristine BC. A similar trend of adsorption capacity was found in milled derivatives of tested adsorbents, with the highest adsorption capacity of HA-MBC for Cd followed by HARP-MBC and RP-WMBC. Additionally, the presence of plenty of surface functional groups on the adsorbent's surface (Figure S1) indicated that the adsorption of Cd was mainly controlled by the interaction between metal (Cd) ions and oxygenated surface functional groups on the adsorbents [54]. Additionally, the lowest $1/n$ value in HA-BC (0.39), HARP-BC (0.39), RP-BC (0.37), HA-MBC (0.56), HARP-MBC (0.56), and RP-WMBC (0.57) showed favorable inter-layer chemical adsorption on Cd. Higher adsorption of positively charged Cd ions by the addition of HA could be due to the net negative, charged adsorbent surface induced by HA by the addition of acidic carboxylic and hydroxyl functional groups [55]. Moreover, the formation of HA-Cd surface complexes could be responsible for more favorable Cd adsorption in HA-treated adsorbents (un-milled and milled).

Table 3. Parameters derived from Langmuir, Freundlich, and Temkin isotherm models for Cd Cu, Zn, and Pb adsorption onto BC, HA-BC, HARP-BC, RP-BC, MBC, HA-MBC, HARP-MBC, WMBC, and RP-WMBC.

Adsorbent	Langmuir			Freundlich			Temkin		
	Q_e (mg g ⁻¹)	K_L (L g ⁻¹)	R^2	K_F (mg g ⁻¹)	1/n	R^2	B	A	R^2
Cadmium (Cd)									
BC	8.41	0.03	0.96	0.86	0.46	0.99	1484	0.69	0.94
HA-BC	9.28	0.07	0.99	1.68	0.39	0.97	1045	0.79	0.94
HARP-BC	9.14	0.07	0.99	1.49	0.39	0.99	1309	1.1	0.9
RP-BC	9.09	0.07	0.97	1.64	0.37	0.99	1445	1.58	0.91
MBC	26.62	0.01	0.96	1.6	0.6	0.96	1128	3.76	0.8
HA-MBC	30.89	0.09	0.96	1.75	0.56	0.99	569	0.82	0.91
HARP-MBC	27.53	0.02	0.98	1.7	0.55	0.99	853	2.68	0.9
WMBC	26.97	0.06	0.97	1.59	0.56	0.98	827	1.94	0.89
RP-WMBC	24.02	0.03	0.98	1.58	0.59	0.98	829	2.47	0.87
Copper (Cu)									
BC	17.17	0.11	0.93	4.15	0.29	0.99	1251	17.8	0.91
HA-BC	16.42	0.09	0.95	3.64	0.32	0.99	1202	13.1	0.88
HARP-BC	16.17	0.09	0.95	3.63	0.33	0.98	1290	18.72	0.84
RP-BC	16.4	0.12	0.96	4.11	0.31	0.99	1218	19.02	0.89
MBC	21.46	0.11	0.96	6.3	0.29	0.99	1018	36.4	0.91
HA-MBC	18.92	0.09	0.95	5.31	0.28	0.99	1186	44.17	0.9
HARP-MBC	17.34	0.22	0.95	5.91	0.24	0.99	1235	77.29	0.9
WMBC	17.55	0.2	0.95	6.22	0.54	0.99	827	71.94	0.89
RP-WMBC	24.02	0.03	0.96	6.41	0.23	0.99	1217	77.3	0.91
Zinc (Zn)									
BC	4.19	0.12	0.94	1.01	0.31	0.99	2916	0.78	0.91
HA-BC	7.98	0.04	0.97	0.8	0.47	0.99	1499	0.6	0.89
HARP-BC	8.22	0.04	0.97	0.87	0.45	0.99	1497	0.69	0.91
RP-BC	7.19	0.03	0.94	0.78	0.44	0.97	2028	1.02	0.88
MBC	11.78	0.02	0.91	1.1	0.45	0.94	1690	2.01	0.88
HA-MBC	15.34	0.01	0.94	0.71	0.58	0.97	1261	2.8	0.81
HARP-MBC	10.94	0.05	0.91	1.69	0.38	0.97	1527	3.12	0.83
WMBC	11.3	0.03	0.96	1.1	0.45	0.98	1500	2.47	0.83
RP-WMBC	18.14	0.01	0.95	0.76	0.57	0.96	1317	3.18	0.8
Lead (Pb)									
BC	11.13	0.06	0.86	3.44	0.35	0.97	1093	9.36	0.95
HA-BC	12.67	0.28	0.91	4.02	0.29	0.99	1241	12.64	0.95
HARP-BC	14.83	0.48	0.92	4.48	0.26	0.99	1267	16.8	0.97
RP-BC	13.7	0.33	0.92	4.53	0.28	0.99	1126	13.16	0.97
MBC	15.61	0.28	0.9	6.3	0.28	0.99	942	25.22	0.96
HA-MBC	17.47	0.51	0.88	5.48	0.27	0.98	999	18.34	0.95
HARP-MBC	18.85	0.67	0.91	6.57	0.27	0.98	928	22.53	0.96
WMBC	16.56	0.47	0.91	6.38	0.27	0.98	919	22.22	0.96
RP-WMBC	18.41	0.58	0.93	6.42	0.25	0.98	894	33.01	0.95

BC = Biochar, HA-BC = Humic acid-modified biochar, HARP-BC = Humic acid and rock phosphate-modified biochar, RP-BC = Rock phosphate-modified biochar, MBC = Ball-milled biochar, HA-MBC = Humic acid-modified ball-milled biochar, ARP-MBC = Humic acid and rock phosphate-modified ball-milled biochar, WMBC = Ball-milled biochar with water, RP-WMBC = Rock phosphate-modified ball-milled biochar with water.

Copper (Cu)

The adsorption of Cu on the tested adsorbents was explained by the application of adsorption isotherm models on experimental data (Figure S4) and (Table 3). Among employed isotherm models, Freundlich was the best-suited model with the highest R^2 value (0.99), followed by Langmuir ($R^2 = 0.96$). For un-milled variants of biochar, pristine BC showed a slightly higher adsorption capacity than HA- and RP-modified BCs, while

among milled variants, RP-WMBC and MBC showed the highest adsorption in both Langmuir (24.02 and 21.46 mg g⁻¹, respectively) and Freundlich models (6.41 and 6.30 mg g⁻¹, respectively). In comparison to RP-modified BCs, slightly lower adsorption was found in HA-modified BCs. The best-suited Freundlich model indicated that Cu adsorption on biochar surface could be due to chemical interaction between Cu ions and BC. The higher adsorption capacity of milled variants of BC indicated a positive impact of ball milling on BC performance in removing heavy metals. Ball milling induced more mesoporous structures in BC, which provided more void surface structures to enhance metals entrapment and, ultimately, higher removal after adsorbate an adsorbent interaction in an aqueous solution [56]. Additionally, a lower value of K_L (rate constant) of HA-modified and RP-modified un-milled and milled BCs showed enhanced adsorption capacity of these adsorbents against chemically unmodified biochars. Similar results of favorable adsorption of Cu were noted by Martins et al. [57] using phosphorus-modified and magnetized BC for Cu and Pb adsorption. Moreover, modification with HA and RP resulted in reduced pH in the range of 5.13–6.41 units (Table 3) which is a favorable pH range for Cu adsorption [58]. Previously, a higher adsorption capacity of Cu by banana peel-derived BC was reported, which could be due to plenty of oxygenated surface functional groups, higher CEC, and net negative surface charge [59].

Zinc (Zn)

The experimental data of Zn adsorption were analyzed by commonly used adsorption isotherms models. The relationship between the equilibrium concentration of Zn in the solution phase and adsorbed Zn on biochar was illustrated and explained using adsorption isotherm models (Figure S5 and Table 3). Observed parameters of adsorption isotherms stated the Freundlich model as the best-suited adsorption model with the highest R^2 (0.99) value, followed by the Langmuir model ($R^2 = 0.97$). Ball milling of BCs showed promising effects on Zn adsorption, and maximum adsorption was found by RP-WMBC (18.14 mg g⁻¹), followed by HA-MBC (15.34 mg g⁻¹) and MBC (11.78 mg g⁻¹). In addition, the heterogeneity coefficient (1/n) was in the range of 0–1 for all the tested BCs, showing favorable adsorption [60]. Higher adsorption capacity of chemically modified biochar with RP and HA modification indicated the positive impact of modification, which was further endorsed by ball milling. Previously, Bogusz et al. [61] found the maximum adsorption of 40.2 mg g⁻¹ for Zn using rice straw BC, while Zhao et al. [62] found Zn adsorption of 43.1 mg g⁻¹ using wheat straw BC and Park et al. [63] found an adsorption capacity of 11.2 mg g⁻¹ using chicken manure BC for Zn. The better fit of the Freundlich model described the fact that Zn adsorption could be inner layer chemical adsorption controlled by various mechanisms, including surface complexation, multilayered adsorption, and heterogeneous layered adsorption.

Lead (Pb)

The adsorption efficiency of applied adsorbents for Pb was analyzed. Among all the applied adsorbents, ball-milled BCs showed comparatively higher adsorption rates against un-milled biochars (Table 3) and (Figure S6). Maximum adsorption was found in HARP-MBC (18.85 mg g⁻¹), followed by RP-WMBC (18.41 mg g⁻¹) and HA-MBC (17.47 mg g⁻¹), which might be due to surface degradation and the addition of further mesopores on adsorbents surface by mechanical action of ball milling. On the other hand, the adsorption capacity of un-milled biochar for Pb was found to be at its maximum in HARP-BC (14.83 mg g⁻¹), followed by RP-BC (13.70 mg g⁻¹) and HA-BC (12.67 mg g⁻¹). The higher adsorption efficiency of HA BCs could be due to the presence of plenty of surface functional groups on HA-treated BC, which provides a number of potentially active sites for metals ion binding and, consequently, increases Pb adsorption [64]. The higher adsorption capacity of HARP-MBC, RP-WMBC, and HA-MBC was further endorsed by BET analysis of these adsorbents, indicating a higher surface area which ultimately favored the adsorption of Pb by these adsorbents. Adsorbed metal ions could make complexes

through chemical interaction with cationic metal ions attached to surface functional groups. Likewise, the enhanced adsorption capacity of milled derivatives of tested BCs was mainly due to enhanced surface functional groups, ultrafine surface area, and the addition of more mesoporous by mechanical milling effects, which provide metal ions with more surface and inter-layer diffusion [23]. In another study, Cao et al. [25], while investigating ball milling effects on wheat straw biochar for Pb adsorption, found that ball milling effectively improved Pb adsorption (134.68 mg g^{-1}) by improving surface and structure properties and the addition of large surface pore volume for better diffusion and binding of metal ions on surface active sites. Chen et al. [65] found plenty of oxygenated surface functional groups in phosphorus-treated BC, which enhanced Pb adsorption by > 5 times more than pristine BC. Zhao et al. [66] reported that treating BC with phosphorus has optimized its pH in the 5.5–6.5 range, which consequently enhanced Pb adsorption by many folds. Additionally, adsorption parameters were further analyzed by applying different adsorption models to find out the adsorption mechanism (Figure S6). The Langmuir model explains equal adsorption ability of all adsorption sites on a homogeneous surface of adsorbent with no mutual interaction among adsorbent molecules. Conversely, the Freundlich model describes adsorption on heterogeneous adsorbent surfaces, which shows higher adsorption at increasing adsorbent dose [44]. Temkin assumes linear adsorption, which indicates a gradual decrease in adsorption by occupying adsorption sites with the adsorbate [67]. Calculated parameters for Pb adsorption are described in Table 3, which shows that Freundlich and Temkin models were fitted better than Langmuir models with average R^2 values of 0.98, 0.95, and 0.90, respectively. The Freundlich isotherm model predicted $1/n$ values were below unity for all the tested adsorbents, indicating a great affinity of all adsorbents to extract and bind Pb from aqueous solution. Similar to Q_e values, an increasing trend of sorption capacity constant (K_F) values was found by HARP-MBC (6.57), followed by RP-WMBC (6.42) and WMBC (6.38), indicating a higher adsorption capacity of these adsorbents than other tested adsorbents. Additionally, higher rate constant (K_L) values of HARP-MBC (0.67) and RP-WMBC (0.58) indicated a greater adsorption-to-desorption ratio along with a higher surface affinity for metal ions [68].

3.3. Kinetics Adsorption

3.3.1. Cadmium (Cd)

A kinetics study of Cd adsorption by employed adsorbents (pristine biochars, humic acid, and rock phosphate-modified BCs and their respective ball-milled derivatives) revealed rapid adsorption in the beginning, which later moved to equilibrium after 8 h (Figure 2). Among un-milled derivatives of biochar, HA-BC showed quick adsorption initially and overall higher adsorption capacity, followed by HARP-BC and RP-BC. Around 92%, 88%, 91%, and 89% of Cd was adsorbed by added adsorbents (BC, HA-BC, HARP-BC, and RP-BC, respectively) in the first 8 h, followed by slow equilibrium in 24 h. A similar trend of adsorption was found in milled BCs, where 88%, 89%, 93%, 92%, and 90% of Cd was completely adsorbed by milled derivatives of employed biochars (MBC, HA-MBC, HARP-MBC, WMBC, and RP-WMBC, respectively). The initially quick adsorption indicated the mass transfer of adsorbate (Cd) on the adsorbent's surface, which later diffused on active sites, and gradually filling of active sites leading to the final equilibrium stage of adsorption [51]. The adsorption of Cd by adsorbents was further investigated by applying different kinetics models to observe the adsorption rate and possible mechanism of adsorption. Among applied kinetics models, pseudo-second-order was fitted well to experimental data ($R^2 = 0.99$), followed by power function ($R^2 = 0.98$) and intraparticle diffusion ($R^2 = 0.91$) (Table 4). Higher rate constant values of RP-BC (0.052) and RP-WMBC (0.160) showed quick initial adsorption and early equilibrium with a rock phosphate-modified biochar. Generally, the first-order model described the physical adsorption of adsorbate on the adsorbent's surface, while the pseudo-second-order model endorsed chemical or physiochemical adsorption [69]. In the current study, pseudo-second-order was the best-suited kinetics model indicating the chemical adsorption of Cd.

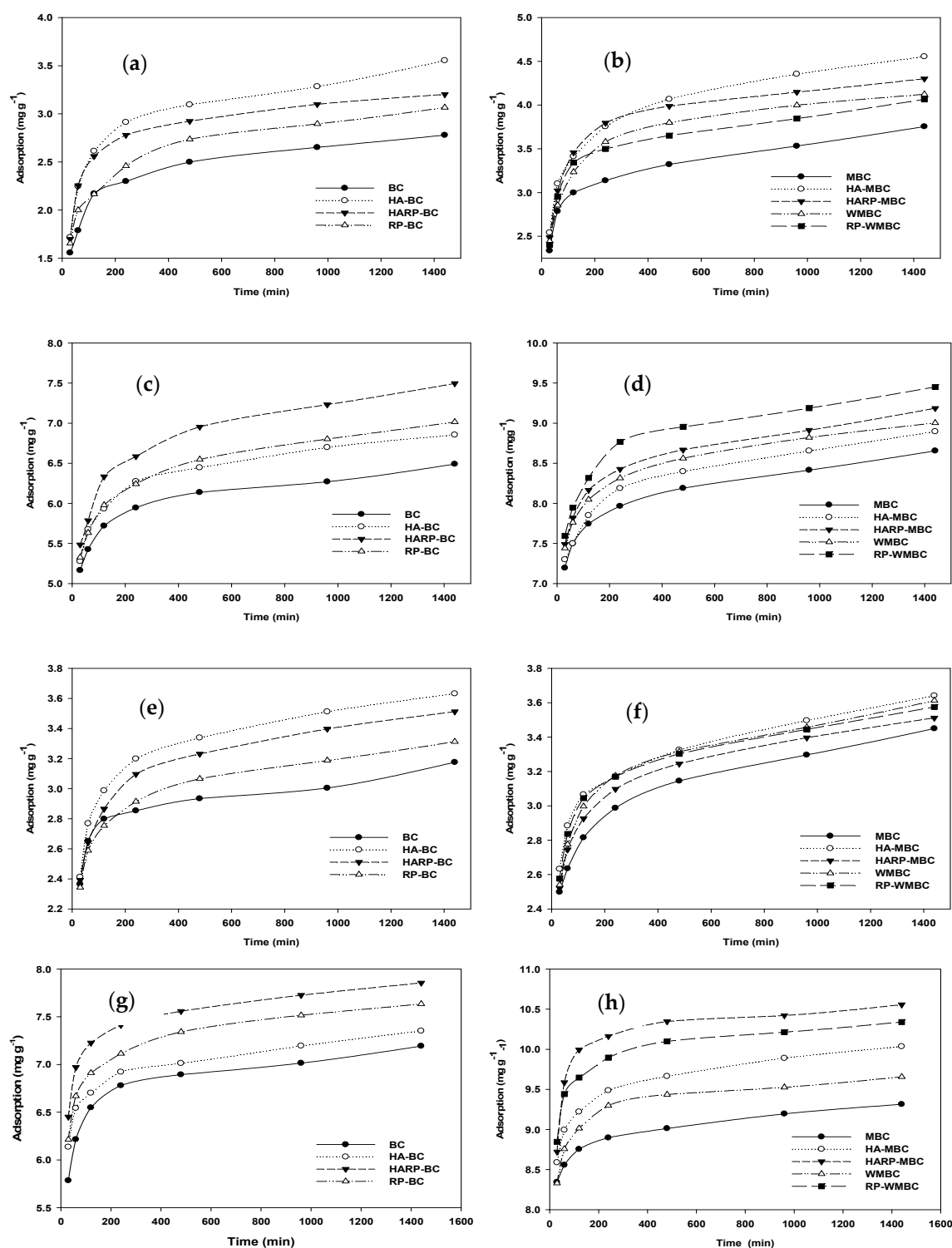


Figure 2. Adsorption kinetics of Cd (a,b), Cu (c,d), Zn (e,f), Pb (g,h) by conocarpus-derived biochar, its modified and milled derivatives. (BC = Biochar, HA-BC = Humic acid-modified biochar, RP-BC = Rock phosphate-modified biochar, HARP-BC = Humic acid and rock phosphate-modified biochar, MBC = Ball-milled biochar, HA-MBC = Humic acid-modified-ball-milled biochar, HARP-MBC = Humic acid and rock phosphate-modified ball-milled biochar, WMBC = Ball-milled biochar with water RP-WMBC = Rock phosphate-modified ball-milled biochar with water).

Table 4. Derived parameters of kinetics for Cd, Cu, Zn, and Pb adsorption onto BC, HA-BC, HARP-BC, RP-BC, MBC, HA-MBC, HARP-MBC, WMBC, RP-WMBC.

Cadmium (Cd)												
Adsorbents	First-Order		Pseudo-Second-Order				Intraparticle-Diffusion			Power Function		
	k_1	R^2	k_2'	q_e	h	R^2	k_{id}	C	R^2	k_f	b	R^2
BC	0.0003	0.72	0.008	2.82	0.07	0.99	0.034	1.612	0.87	0.145	0.004	0.95
HA-BC	0.0004	0.71	0.006	3.59	0.07	0.99	0.048	1.882	0.85	0.169	0.077	0.98
HARP-BC	0.0003	0.63	0.011	3.25	0.09	0.99	0.038	1.934	0.78	0.145	0.163	0.90
RP-BC	0.0003	0.78	0.052	2.51	0.06	0.99	0.037	1.679	0.91	0.153	0.034	0.98
MBC	0.0002	0.77	0.093	3.05	0.10	0.99	0.040	2.441	0.89	0.108	0.541	0.95
HA-MBC	0.0003	0.75	0.005	4.63	0.11	0.99	0.055	2.653	0.89	0.141	0.619	0.93
HARP-MBC	0.0003	0.64	0.069	4.40	0.14	0.99	0.048	2.706	0.80	0.132	0.549	0.92
WMBC	0.0003	0.77	0.099	3.11	0.12	0.99	0.047	2.563	0.85	0.130	0.509	0.95
RP-WMBC	0.0002	0.67	0.160	3.87	0.12	0.99	0.042	2.619	0.81	0.119	0.562	0.91
Copper (Cu)												
BC	0.0001	0.77	0.009	6.50	0.37	0.99	0.037	5.197	0.87	0.056	1.462	0.95
HA-BC	0.0002	0.75	0.008	6.89	0.36	0.99	0.044	5.349	0.85	0.065	1.463	0.98
HARP-BC	0.0002	0.78	0.01	7.54	0.30	0.99	0.058	5.474	0.78	0.080	1.440	0.91
RP-BC	0.0002	0.80	0.050	7.50	0.31	0.99	0.049	5.316	0.91	0.070	1.444	0.98
MBC	0.0001	0.83	0.094	7.41	0.55	0.99	0.041	7.193	0.89	0.045	1.826	0.94
HA-MBC	0.0001	0.81	0.007	8.92	0.52	0.99	0.047	7.240	0.89	0.051	1.813	0.93
HARP-MBC	0.0001	0.80	0.062	9.95	0.54	0.99	0.047	7.499	0.80	0.050	1.850	0.92
WMBC	0.0001	0.80	0.102	8.40	0.58	0.99	0.045	7.449	0.85	0.048	1.851	0.95
RP-WMBC	0.0001	0.76	0.140	9.01	0.54	0.99	0.052	7.628	0.81	0.055	1.850	0.94
Zinc (Zn)												
BC	0.0002	0.71	0.015	2.17	0.15	0.99	0.019	2.464	0.82	0.064	0.689	0.95
HA-BC	0.0002	0.72	0.010	3.66	0.13	0.99	0.033	2.511	0.86	0.098	0.595	0.98
HARP-BC	0.0002	0.75	0.01	3.55	0.12	0.99	0.031	2.434	0.89	0.096	0.574	0.90
RP-BC	0.0002	0.77	0.091	3.18	0.13	0.99	0.027	2.385	0.90	0.084	0.593	0.98
MBC	0.0002	0.84	0.127	3.97	0.12	0.99	0.028	2.459	0.95	0.082	0.637	0.99
HA-MBC	0.0002	0.81	0.010	4.66	0.14	0.99	0.027	2.661	0.92	0.078	0.727	0.93
HARP-MBC	0.0002	0.78	0.106	4.13	0.13	0.99	0.028	2.545	0.91	0.082	0.666	0.98
WMBC	0.0002	0.77	0.152	3.96	0.13	0.99	0.030	2.575	0.90	0.086	0.664	0.95
RP-WMBC	0.0002	0.76	0.243	3.76	0.15	0.99	0.027	2.636	0.87	0.079	0.710	0.90
Lead (Pb)												
BC	0.0001	0.65	0.010	7.20	0.54	0.99	0.036	5.961	0.77	0.051	1.610	0.93
HA-BC	0.0001	0.73	0.011	7.36	0.57	0.98	0.031	6.252	0.83	0.042	1.692	0.96
HARP-BC	0.0001	0.66	0.01	7.88	0.65	0.99	0.035	6.253	0.78	0.046	1.740	0.93
RP-BC	0.0002	0.50	0.010	7.67	0.56	0.99	0.038	6.351	0.85	0.050	1.682	0.96
MBC	0.0001	0.64	0.012	9.33	1.05	0.98	0.027	8.364	0.90	0.027	2.034	0.99
HA-MBC	0.0001	0.63	0.009	10.07	0.89	0.99	0.039	8.676	0.88	0.038	2.034	0.93
HARP-MBC	0.0001	0.71	0.011	10.58	1.27	0.99	0.042	9.181	0.65	0.042	2.068	0.96
WMBC	0.0001	0.80	0.012	9.68	1.13	0.99	0.035	8.501	0.69	0.036	2.018	0.99
RP-WMBC	0.0001	0.75	0.011	10.37	1.17	0.99	0.038	9.080	0.78	0.036	2.081	0.98

BC = Biochar, HA-BC = Humic acid-modified biochar, HARP-BC = Humic acid and rock phosphate-modified biochar, RP-BC = Rock phosphate-modified biochar, MBC = Ball-milled biochar, HA-MBC = Humic acid modified ball-milled biochar, ARP-MBC = Humic acid and rock phosphate-modified ball-milled biochar, WMBC = Ball-milled biochar with water, RP-WMBC = Rock phosphate-modified ball-milled biochar with water.

3.3.2. Copper (Cu)

Relatively quicker adsorption was observed in the beginning, which later reached equilibrium after 8 h (Figure 2). The HARP-BC showed an overall higher adsorption capacity, followed by RP-BC and HA-BC. Around 93%, 92%, 91%, and 94% of Cu was adsorbed by added adsorbents (BC, HA-BC, HARP-BC, and RP-BC, respectively) in the first 8 h, followed by slow equilibrium in 24 h. A similar trend of adsorption was found in milled BCs, where more than 94% Cu was completely adsorbed by milled derivatives

of employed BCs (MBC, HA-MBC, HARP-MBC, WMBC, and RP-WMBC, respectively). Adsorption of Cu followed a three-stage process; (i) quick adsorption in the beginning due to more available active sites, (ii) slow adsorption towards progressive equilibrium, and (iii) attaining adsorption equilibrium [70]. Generally, quick adsorption, in the beginning, could be due to more available active sites on the adsorbent's surface and more mass transfer of adsorbate (Cu) from the solution phase to solid adsorbent [71], whereas progressive saturation of active sites on the adsorbent lead to a final equilibrium. The adsorption of Cu by adsorbents was further investigated by applying different kinetics models to observe the adsorption rate and possible mechanisms of adsorption. Among applied kinetics models, the pseudo-second-order model was fitted well to experimental data ($R^2 = 0.99$), followed by power function ($R^2 = 0.98$) and intraparticle diffusion ($R^2 = 0.91$). Higher rate constant value of RP-BC (0.050) and RP-WMBC (0.140) showed quicker initial adsorption and early equilibrium by RP biochar, while un-milled and milled variants of HA-modified biochar showed higher adsorption constants ($k_f = 0.065$ and 0.051) and a higher rate of adsorption under applied power function kinetics model. Overall, the applied kinetics model described the fact that Cu adsorption could be the function of mass transfer and chemisorption of the adsorbent's surface [72].

3.3.3. Zinc (Zn)

Similar to Cu and Cd, the adsorption of Zn initially followed the pattern of quick adsorption, which later diffused into the inner layers of the adsorbent and finally reached equilibrium. Among the un-milled derivatives of biochar, HA-BC showed the quickest adsorption initially and overall higher adsorption capacity, followed by HARP-BC and RP-BC. In all employed adsorbents, more than 90% adsorption was attained in the first 8 h, which later moved to equilibrium after 24 h of contact time. Among all un-milled and milled adsorbents, HA-modified BCs showed a higher adsorption capacity, followed by HARP- and RP-modified BCs. The adsorption of Zn followed quick bulk mass transfer initially due to higher available active sites on the adsorbent's surface, followed by the inter-layer diffusion of adsorbate molecules into a layer of adsorbents by quick agitation of adsorbate and adsorbent solution and finally complete adsorption by chemisorption [72]. Adsorption of Zn by adsorbent was further investigated by applying different kinetics models to observe the adsorption rate and possible mechanism of adsorption. Among applied kinetics models, the pseudo-second-order model fit best to experimental data ($R^2 = 0.99$), followed by power function ($R^2 = 0.98$) and intraparticle diffusion ($R^2 = 0.95$) (Table 4). Applied adsorption models indicated that chemisorption was the rate-limiting factor in Zn adsorption, while adsorption was also found to be multilayer sorption owing to the heterogeneous surface of BCs, which supported intraparticle diffusion of adsorbate molecules on adsorbents [73].

3.3.4. Lead (Pb)

Adsorption capacity with time of all produced and modified BCs is described in (Figure 2), showing rapid adsorption initially, which comes to equilibrium after 8 h until 24 h is reached. The initially higher rate of adsorption could be due to the presence of more available active sites on the adsorbent's surface, which were equipped by Pb ions, a condition that later led to stable and equilibrium state adsorption. Our findings showed the higher adsorption capacity of modified BCs compared to pristine biochar. Higher initial sorption of Pb by HA- and RP-treated BCs could be due to the presence of plenty of oxygenated surface functional groups, more available active sites to bind metal (Pb) ions, and the optimized pH of adsorbents [66]. Additionally, as compared to un-milled BCs, milled BCs showed a higher adsorption rate, which could be due to ball milling effects. Ball milling resulted in the destruction and generation of more mesopores on the adsorbent's surface, which enhanced their adsorption capacity [25]. In a previous study, Lyu et al. [22] recorded a prominent increase in the adsorption capacity ($230\text{--}650\text{ mmol kg}^{-1}$) of sugarcane-, bamboo-, and wood-chip-derived ball-milled BCs for Ni against their un-

milled derivative ($26\text{--}110\text{ mmol kg}^{-1}$). Cao et al. [25] and Zhang et al. [74] reported similar results of higher adsorption of milled biochar for Pb (134.8 mg g^{-1}) and other organic pollutants. Additionally, our results showed the acidification of biochar (HA-BC and HA-MBC), which enhanced Pb adsorption on the biochar's surface. Zhou et al. [55] reported the positive impact of HA-modified BC in decreasing Pb contents to 1.28 mg kg^{-1} , which were 200 mg kg^{-1} in Pb-contaminated soil. To better understand the adsorption characteristics, the calculated experimental data were further subjected to different kinetics models (Table 4). The higher rate constant and R^2 value (0.99) indicated pseudo-second-order as the best-suited kinetics model, followed by power function. The results showed that Pb adsorption on the adsorbent's surface was equally affected by the sorption capacity of adsorbents (BCs) and applied adsorbate concentrations [75]. The higher rate constant and regression of intraparticle-diffusion models indicate higher adsorption, owing to the porous surface of adsorbents. Our results described the mass transfer of Pb from the aqueous solution to the adsorbent's surface, followed by the surface diffusion of Pb [76]. Based on the highest rate constant and R^2 values, pseudo-second-order, and power function were found to be the best-fitted models for Pb adsorption on the tested adsorbents. The best-fitted kinetics model suggested that Pb adsorption on tested adsorbents could be controlled by multiple mechanisms, such as inner layer diffusion, surface adsorption, and chemisorption.

3.4. Mechanism for Metals Adsorption

The experimental data generally favored electrostatic interaction between positively charged metal ions and negative surface-charged adsorbents. Inter-layer chemical adsorption was also involved, which was further explained by adsorption isotherm and kinetics studies. The mechanism of Cd, Cu, Zn, and Pb adsorption on the tested adsorbents' surface was explained by the surface characteristics of the adsorbents and the applied isotherm and kinetics models. The initial adsorption of cationic heavy metals could be due to electrostatic interaction between the net negative surface charge of biochar (alkaline pH) and positively charged metal ions [77]. The presence of aromatic carbon structures and additional oxygen-containing functional groups on the BC's surface generated by ball milling indicated the surface complexation of metal with carboxy and hydroxy groups [25]. The best-suited Langmuir model recognized the monolayer adsorption of metal on the adsorbent's surface, which could be due to electrostatic interaction between oppositely charged ions and the adsorbent's surface [78]. Additionally, Freundlich isotherm and kinetics models explained the inter-layer diffusion and fixation of metal ions in adsorbent layers resulting from chemical interaction between metal and adsorbents. The presence of acidic and oxygenated surface functional groups endorsed interaction between surface functional groups and metal ions by forming surface complexation [79]. Kinetics study revealed the quick initial adsorption by the mass flow of metal in the aquatic phase with the solid adsorbent, which later on gradually moved towards equilibrium by completely occupying active surface sites and inter-layer diffusion of metal ions. Later, metals sorption on the adsorbent's surface could be due to a cationic exchange reaction between metal ions and functional-groups-bounded cationic metal ions [80]. Additionally, as described in the XRD analysis of BCs, the presence of CaCO_3 and $\text{Ca}_3(\text{PO}_4)_2$ might have released inorganic anions (CO_3^{2-} , PO_4^{3-}), which further took part in the precipitation of metal. The production of BC at a higher pyrolysis temperature ($600\text{ }^\circ\text{C}$) supports the active sorption of metal. At higher pyrolysis temperatures, organic compounds were completely carbonized, leading to higher surface areas, which consequently provide more active sites for metal sorption [81]. Higher porosity and a greater number of mesoporous surface structures were confirmed by BET analysis, which favored the higher adsorption capacity of the tested adsorbents and the ultrafine surface structure of BCs via the effects of ball milling, which further facilitated the sorption of metal ions. Previous studies also endorsed the surface complexation mechanism of metal adsorption via oxygen-containing functional groups [82].

4. Conclusions

This study was aimed at exploring adsorptive characteristics and investigating the adsorption efficiency of conocarpus-derived BC and its ball-milled derivatives. Ball milling, as well as modifications with HA- and RP-induced distinctive characteristic differences in BC against its original derivative; these differences mainly include a decline in pH values, enhanced surface porosity, higher surface crystallinity, and additional surface functional groups. Pristine BC was found to be highly alkaline with a pH value of 10.14, while this value decreased to 5.14 in HA-BC and 6.10 in RP-BC. Surface and adsorptive characteristics of milled BCs showed distinguishing variations, including enhanced surface porosity, the addition of oxygen-containing functional groups, and more crystallinity which could be due to the mechanical effects of ball milling. Adsorbents were tested for their adsorption efficiencies for Cd, Cu, Zn, and Pb, and experimental data showed Freundlich and Temkin as the best-fitted adsorption models. Kinetics studies of adsorption by tested adsorbents were favored by pseudo-second-order and power function models. Humic acid and rock phosphate-modified milled BC showed the highest adsorption capacity for Pb adsorption, while rock phosphate-modified milled BC showed the highest adsorption capacity for Cu and Zn, and humic acid-modified BC showed the highest adsorption for Cd (30.89 mg g^{-1}). Our study endorsed that modification of biochar with humic and/or rock phosphate positively impacted metal adsorption, and ball milling enhanced surface porosity, which further increased the adsorption ability of milled BC. Therefore, humic acid and rock phosphate-modified milled biochar could serve as an efficient and cost-effective approach for the removal of heavy metals from contaminated water.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su151411474/s1>. Figure S1: FTIR spectra of conocarpus biochar and its un-milled, milled and modified derivatives (BC = Biochar, MBC = Ball milled biochar, HA-MBC = Humic acid modified ball milled biochar, RP-WMBC = Rock phosphate modified ball milled biochar with water); Figure S2: XRD spectra of conocarpus biochar and its un-milled, milled and modified derivatives (BC = Biochar, HA-BC = Humic acid modified biochar, RP-BC = Rock phosphate modified biochar, HARP-BC = Humic acid and rock phosphate modified biochar, MBC = Ball milled biochar, HA-MBC = Humic acid modified ball milled biochar, HARP-MBC = Humic acid and rock phosphate modified ball milled biochar, WMBC = Ball milled biochar with water, RP-WMBC = Rock phosphate modified ball milled biochar with water); Figure S3: Langmuir (a,b), Freundlich (c,d) and Temkin (e,f) adsorption isotherms of Cd by (a) un-milled adsorbents and (b) milled adsorbents (BC = Biochar, HA-BC = Humic acid modified biochar, HARP-BC = Humic acid and rock phosphate modified biochar, RP-BC = Rock phosphate modified biochar, MBC = Ball milled biochar, HA-MBC = Humic acid modified ball milled biochar, HARP-MBC = Humic acid and rock phosphate modified ball milled biochar, WMBC = Ball milled biochar with water, RP-WMBC = Rock phosphate modified ball milled biochar with water); Figure S4: Langmuir(a,b), Freundlich (c,d) and Temkin (e,f) adsorption isotherms of Cu by (a) un-milled adsorbents and (b) milled adsorbents (BC = Biochar, HA-BC = Humic acid modified biochar, HARP-BC = Humic acid and rock phosphate modified biochar, RP-BC = Rock phosphate modified biochar, MBC = Ball milled biochar, HA-MBC = Humic acid modified ball milled biochar, HARP-MBC = Humic acid and rock phosphate modified ball milled biochar, WMBC = Ball milled biochar with water, RP-WMBC = Rock phosphate modified ball milled biochar with water); Figure S5: Langmuir (a,b), Freundlich (c,d) and Temkin (e,f) adsorption isotherms of Zn by (a) un-milled adsorbents and (b) milled adsorbents (BC = Biochar, HA-BC = Humic acid modified biochar, HARP-BC = Humic acid and rock phosphate modified biochar, RP-BC = Rock phosphate modified biochar, MBC = Ball milled biochar, HA-MBC = Humic acid modified ball milled biochar, HARP-MBC = Humic acid and rock phosphate modified ball milled biochar, WMBC = Ball milled biochar with water, RP-WMBC = Rock phosphate modified ball milled biochar with water); and Figure S6: Adsorption isotherms of Pb by conocarpus derived biochar, its modified and milled derivatives. Figure 2a,b (Langmuir), c,d (Freundlich) and e,f (Temkin) (BC = Biochar, HA-BC = Humic acid modified biochar, RP-BC = Rock phosphate modified biochar, HARP-BC = Humic acid and rock phosphate modified biochar, MBC = Ball milled biochar, HA-MBC = Humic acid modified ball milled biochar, HARP-MBC = Humic acid and rock phosphate modified ball milled biochar, WMBC = Ball milled biochar with water, RP-WMBC = Rock phosphate modified ball milled biochar with water).

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Abbreviations

Abbreviation	Definition
CEC	Cation exchange capacity
EC	Electrical conductivity
BC	Biochar
HA	Humic acid
HA-BC	Humic acid-modified biochar
RP	Rock phosphate
RP-BC	Rock phosphate-modified biochar
HARP-BC	Humic acid and rock phosphate-modified biochar
MBC	Ball-milled biochar
WMBC	Ball-milled biochar with water
HA-MBC	Humic acid-modified ball-milled biochar
RP-WMBC	Rock phosphate-modified ball-milled biochar with water
HARP-MBC	Humic acid and rock phosphate-modified ball-milled biochar
SEM	Scanning electron microscopy
XRD	X-ray diffraction
FTIR	Fourier transformation infrared spectroscopy
BET	Brunauer–emmett–teller
ICP-OES	Inductively coupled plasma optical emission spectroscopy
LSD	Least significance difference

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