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Employment of Cannabis sativa biochar to improve soil nutrient pool and metal immobilization

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Soil pollution with heavy metals has become a global issue because of anthropogenic activities causing gradual loss of soil nutrients and fertility, thus, reducing agricultural production. Biochar is recommended as an organic and environment-friendly option to address the issue of nutrient deficiency and heavy metal pollution. The present study was performed with biochar derived from Cannabis sativa to surplus soil nutrient pool and heavy metal immobilization. The characterization through scanning electron microscopy (SEM) revealed that biochar was brittle, porous, alkaline, and labile in nature. The elemental composition of biochar was carbon (75.3%), oxygen (19.2%), calcium (3.9%), potassium (1.5%), and chlorine (0.08%) determined by energy dispersive X-ray spectroscopy. Fourier transform infrared (FTIR) spectroscopy revealed the occurrence of carbonyl group, phenols, and alcohols in biochar derived from Cannabis sativa. The soil was spiked with lead and cadmium salt solution (25 ppm and 250) and incubated for 30 days. It was found that biochar amendments (1% = BC1 and 5% = BC5) significantly ($p < 0.05$) increased the soil physicochemical properties such as pH, electrical conductivity (EC), oxidizable organic carbon (OC), total organic carbon (TOC), and organic matter (OM). In the case of BC5, OC increased by 189.86%, TOC increased by 189.13%, and OM increased by 188.68%, as compared to the control. Similarly, soil available nitrogen (AN) and soil available phosphorous improved by 233.3% and 101.79%, respectively, compared to control. On the other hand, BC1 showed a significant reduction ($p < 0.05$) in lead and cadmium concentrations by 45.74% and 56.58%, respectively, in comparison to BC5 and control. In conclusion, we suggest that Cannabis sativa biochar may serve as an effective treatment for enhancing soil fertility and remediation of soil polluted with heavy metals.

KEYWORDS

biochar, pyrolysis, cannabis sativa, heavy metals, total carbon, soil nitrogen

1 Introduction

Soil is not only a substrate for plant growth but also the ultimate sink for organic and inorganic pollutants such as pesticides and heavy metals (Qayyum et al., 2017; Tu et al., 2020). As a consequence of human activities such as mining, oil drilling, waste disposal, industrial operations, and pesticide and metal processing, heavy metal pollution has become a global challenge for sustainable agriculture in recent years (Abbas et al., 2017a; Shen et al., 2018; Juraszek and Piasecka, 2020). Once heavy metals enter the soil environment through irrigation with wastewater or land application of contaminated biosolids, they can induce irreversible damage to plant growth and enter the human body through ingestion of edible plants parts, causing inactivation of enzymes and destruction of proteins (Hamzenejad Taghlidabad and Sepehr, 2018). In addition to the tremendous amount of heavy metal pollution, soils all over the world are being overexploited for food production, raising concerns for the agricultural ecosystem.

The extensive use of inorganic fertilizers to replenish soil nutrients is disregarded as a cause of heavy metal accumulation in agricultural soil. Continuous cropping practices lead to gradual loss of soil fertility that will promote the widespread use of inorganic fertilizers (Sandhu et al., 2017) that contain essential nutrients along with trace quantities of heavy metals (Iheanacho et al., 2017). Therefore, the inevitable use of chemical fertilizers is now recognized as an unsustainable agricultural strategy because it is causing rapid soil organic matter mineralization and addition of heavy metals, posing a threat to the soil environment (Naeem et al., 2018) (Barrow, 2012). Ultimately, there is a need to reduce the risk of heavy metals by limiting the bioavailability in the food chain *via* metal absorption and their accumulation in the sink (Juraszek and Piasecka, 2020).

Organic fertilizers, including compost and manure, were created as alternatives to chemical fertilizers; nevertheless, despite their eco-friendliness, they include pathogens, pharmaceuticals, and organic waste and have the potential to contaminate streams and groundwater with nutrients (Barrow, 2012; Al-Wabel et al., 2017). Due to their organic nature, pharmaceuticals and organic waste were readily decomposed by soil microbes, whereas heavy metal removal requires costly and risky physical and chemical processes such as precipitation, ion exchange, adsorption, and electro-coagulation. Adsorption is a fast and cost-effective method for recovering heavy metal polluted soils (Park et al., 2015).

Considering the situation, a more resistant organic amendment called "agrichar" or "biochar" that may survive in soils for thousands of years (Naeem et al., 2018) has received particular attention for treating soil nutrient deficit and metal pollution *via* adsorption (Cao et al., 2011; Ahmad et al., 2017; Li F. et al., 2021). Biochar is an organic substance that is typically manufactured from a range of

biomass, such as wood, branches, leaves, agricultural waste (Han et al., 2013), shells, husk, and animal and poultry waste (Yang et al., 2017; Hamzenejad Taghlidabad and Sepehr, 2018). The biomass feedstock can be pyrolyzed at a high temperature with limited oxygen. The resulting material (biochar) is highly porous and stabilized and can be utilized as an adsorbent due to the large surface area, microporosity, functional groups, and hydrophobicity (Omidi et al., 2020). Biochar is regarded as a soil conditioner because it influences soil properties such as high water holding and cation exchange capacity, which helps in retaining nutrients and microbial activity in the soil (Fellet et al., 2011; Wu et al., 2017; Rizwan et al., 2018).

The characteristics and efficiency of biochar vary depending on the feedstock and pyrolysis temperature (Tu et al., 2020; Manori et al., 2021). The pyrolysis temperature is an important factor in determining the adsorption capacity of heavy metals in each feedstock (Ding et al., 2014; Lian et al., 2020). For instance, biochar produced at higher temperatures performed better for metal immobilization than those produced at lower temperatures (Paz-Ferreiro et al., 2014; Shu et al., 2016; Kavitha et al., 2018; Wei et al., 2019). It was also reported that oxygen-containing functional groups tend to be formed at lower pyrolysis temperatures, while aromatic structures and alkaline minerals are always formed at higher temperatures (Yang et al., 2019). Because of its porous structure, biochar is perfect for adsorption and has been effectively used to stabilize different pollutants in soil (Gholizadeh and Hu, 2021).

Cannabis is an annual flowering herb that grows rapidly in large areas; it is extensively cultivated and used in central Asia. Cannabis is a moderately common plant that grows abundantly in northern Pakistan. Although the cultivation, possession, and distribution of cannabis are prohibited in Pakistan by the National Act of 1997, however, this plant offers a broad variety of potential uses and grows abundantly in the wild. Cannabis has hitherto been utilized exclusively for medical research, but there are several opportunities to use it as an energy crop, an absorbent, insulation, pyrolysis material, and activated biomass, all of which improve the soil systems. Recognizing the diverse application and the potential for turning a wild-grown plant into a useful product, Pakistan's Federal Government allowed the legalization of Cannabis production, primarily for scientific, technological, and industrial research purposes. In this study, *Cannabis sativa* was used to prepare biochar, and this activated product was used as soil conditional and metal adsorbent in contaminated soil.

2 Materials and methods

2.1 Biochar preparation

Cannabis sativa, commonly known as industrial hemp, was collected from the roadside of Islamabad. The plant biomass,

including the stems and branch of *C. staiva*, was collected, air-dried to remove moisture, chopped into 2–3-inch pieces, and further dried in an oven at 105°C for 1 h to remove any remaining moisture (Qadeer et al., 2014). Healthy dried stems were used for the biochar preparation.

The oven-dried *Cannabis sativa* biomass was pyrolyzed at 450°C for 20 min in a muffle furnace (Qadeer et al., 2014). After 20 min of pyrolysis, the material was allowed to cool at room temperature. The obtained black and brittle biochar was weighed and placed in an airtight plastic jar with silica gel (for moisture absorption) till further use. The biochar was ground to powder using a pestle and mortar and sieved to 0.5-mm for characterization and even distribution in the soil (Xu et al., 2013).

2.1.1 Physicochemical analysis

The prepared biochar was analyzed for physico-chemical parameters. pH and EC of the prepared biochar were measured using calibrated multi-parameter PCSTestr™ 35. Powdered biochar solution was prepared by using deionized water in a 1:20 solid: deionized water ratio (Hamdani et al., 2017). Conversion efficiency or yield of biochar was determined using the following formula:

$$\text{Conversion Efficiency or Yield (\%)}$$
$$= \frac{\text{Weight of biochar collected after pyrolysis (kg)}}{\text{Weight of feedstock used for pyrolysis (kg)}} \times 100.$$

Weights were recorded prior to and after pyrolysis for calculating the yield (Hamdani et al., 2017).

To calculate the bulk density, the biochar sample was placed in an oven at 105°C for 24 h. Afterward, it was noted that the weight of the oven-dried biochar occupied 50 ml cylinder volume, and it was divided by the volume of the cylinder used (Qadeer et al., 2014; Khater, 2015). Bulk density was calculated using the formula given by Dawood et al. (2017):

$$\text{Bulk Density} = \frac{\text{Mass of dry sample (g)}}{\text{Total volume used (cm}^3)}. \quad (2)$$

2.1.2 Proximate analysis

The moisture content of the biochar was calculated by drying the biochar in a muffle furnace for 10 min at 750°C. It was then taken out of the furnace and allowed to cool down at room temperature, after which it was weighed (ASTM, 2007). The dried biochar sample was then further placed in oven at 105°C for 2 h. Afterward, it was allowed to cool down to room temperature and weighed again (Batool et al., 2015). The moisture content was calculated using the formula given in ASTM D1762-84:

$$MC(\%) = \frac{\text{Weight of air} - \text{dried biochar (g)} - \text{Weight of oven} - \text{dried biochar (g)}}{\text{Weight of air} - \text{dried biochar}} \times 100. \quad (3)$$

The volatile content of the biochar was determined by subjecting the dried biochar to 550°C in a muffle furnace for 3 h (Waqas et al., 2018). The volatile content was calculated using the formula given in ASTM (2007):

$$VC(\%) = \frac{\text{Biochar weight dried at 105°C (g)} - \text{Biochar weight dried at 550°C (g)}}{\text{Biochar weight dried at 105°C (g)}} \times 100. \quad (4)$$

To determine the ash content, the biochar sample was weighed and placed in a crucible uncovered. It was then heated to 800°C for 4 h in a muffle furnace (Batool et al., 2015). After that, it was removed from the furnace, cooled to room temperature, and weighed again. The ash content was calculated according to the following formula (Waqas et al., 2018):

$$AC(\%) = \frac{\text{Weight of biochar ash (g)}}{\text{Weight of biochar used for heating (g)}} \times 100. \quad (5)$$

Fixed carbon was calculated by the difference in mass using the following formula (Lam et al., 2018):

FC (%) = 100—Ash content (%)—Moisture content (%)—Volatile content (%)

2.1.3 Instrumental analysis

Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) was used to determine the surface morphology (porosity, pore size, and pore shape) and elemental composition of the prepared biochar (Xu et al., 2013; Waqas et al., 2018). Tescan Vega 3 scanning electron microscope with Oxford EDX detector at the National University of Science and Technology (CASEN-NUST) was used to perform SEM-EDX.

In order to determine the surface functional groups, Fourier transform infrared spectroscopy (FTIR) was employed (Xu et al., 2013; Waqas et al., 2018). About 0.7–1 mg of powdered biochar and 100 mg of spectroscopic grade potassium bromide (KBr) were mixed and pressed in a hydraulic press to form a pellet (Pourret and Houben, 2018). A Perkin Elmer FTIR spectrophotometer at the National University of Science and Technology (SCME-NUST) was used to analyze the prepared KBr and biochar pellets, scanning in the range of 400–4,000 cm^{-1}, with an average of 32 scans and a resolution of 4 cm^{-1} (Waqas et al., 2018). FTIR spectrum obtained was interpreted using already reported data in previous literature (Mohanty et al., 2013).

2.2 Soil collection and background analysis

Soil was collected from a private agricultural farmland area near Chak Shahzad in Islamabad; the cultivator does not apply inorganic fertilizer to the fields. Soil was collected from the top/surface 0–20 cm, air-dried, grounded, and passed through a 2-mm sieve to homogenize the soil sample (Abbas et al., 2017b). To determine the metal (Pb & Cd) background concentration, 5 g of

TABLE 1 Biochar treatments kept at room temperature for 1 month.

Treatments	Composition
Control	Spiked soil with no biochar addition
BC1	Spiked soil with 1% biochar addition
BC5	Spiked soil with 5% biochar addition

air-dried soil was acid digested (HNO_3: HCl; 1:3) to be analyzed through inductively coupled plasma optical emission spectrometry (ICP-OES).

2.2.1 Soil spiking

The air-dried soil was spiked with $Pb(NO_3)_2$ and $Cd(NO_3)_2$ solutions (Bashir et al., 2018; Mehmood et al., 2018), at concentrations of 25 ppm and 250 ppm, respectively, which were nearly four times the average concentrations of Pb and Cd in soils of Islamabad (Faiz et al., 2009). After spiking, the soil was incubated at room temperature ($22 \pm 2°C$) and aged for 15 days to allow adequate exposure of soil particles to metal contamination; the soil pack was occasionally mixed to homogenize the bulk soil (Khalkhaliani et al., 2006). Following this period, the soil was divided equally into three portions (in triplicates) for different treatments/experimental set-up.

2.3 Experimental set-up and periodic soil analysis

A pot experiment was conducted to evaluate the effects of biochar addition on the soil nutrient pool and soil metal immobilization. Incubated soil was shifted into pots with a capacity of 2.5 kg, and all pots were grouped in different treatments of soil biochar combination and control soil. The prepared biochar was added to the pots with spiked soil separately, at two different concentrations, i.e., 1% and 5% (w/w). The pots without any biochar addition were used as the control (Table 1). All the pots were arranged in a complete randomized design and placed in a laboratory at room temperature ($22 \pm 2°C$).

After biochar addition, the field capacity of the soil was calculated, and the overall set-up was maintained at 70% field capacity gravimetrically. The pots were covered with plastic food wrap to avoid loss of moisture; however, small holes were made in them to allow an exchange of gases (Mehmood et al., 2018). The entire experimental set-up was kept at room temperature for a period of 1 month, and all the treatments, along with the control, were set in triplicates (Qadeer et al., 2014; Bashir et al., 2018; Mehmood et al., 2018). Soil samples from each treatment were collected individually and periodically, i.e., at the beginning of the

experimental set-up (time zero) and after an interval of every 10 days, for a period of 1 month. Each time, the samples were taken directly from every treatment and control pots and analyzed in triplicates. None of the samples was used as a composite sample.

2.3.1 pH and electrical conductivity

pH and EC of the biochar amended soil samples and of the control were measured using calibrated multi-parameter PCSTestr™ 35. In a solution of soil:deionized water, at the ratio of 1:5 (Bashir et al., 2018).

2.3.2 Oxidizable organic carbon, total organic carbon, and organic matter

Walkley and Black's (1934) titration method was employed to calculate the organic matter (OM) (Qadeer et al., 2014), total organic carbon (TOC), and oxidizable organic carbon (OC) (Choudhary et al., 2018) present in the soil samples. OC, TOC, and OM were calculated using the following formulae:

$$\text{Oxidizable Organic Carbon}\,(\%) = \frac{(V\text{Blank} - V\text{sample}) \times 0.3 \times M}{\text{Weight of air dried soil (g)}}, \quad (6)$$

where

M = molarity of FAS solution–about 0.5 M.

V_{Blank} = volume of FAS solution required to titrate the blank (ml).

V_{Sample} = volume of FAS solution required to titrate the sample (ml).

$0.3 = 3 \times 10^{-3} \times 100$, where 3 is the equivalent weight of C.

$$\text{Total Organic Carbon}\,(\%) = 1.334 \times \text{Oxidizable Organic Carbon}\,(\%), \quad (7)$$

$$\text{Organic Matter}\,(\%) = 1.724 \times \text{Total Organic Carbon}\,(\%). \quad (8)$$

2.3.3 Soil available nitrogen

Soil available nitrogen (AN) was analyzed using the method described by Arif et al. (2018). In total, 5 g of soil sample and 25 ml of K_2SO_4 were added to a 50 ml centrifuge tube and shaken at 150 rpm for a period of 60 min. A total of 0.5 ml of the extract was taken and mixed with 1 ml of salicylic acid. The mixture was allowed to stand for 10 min, after which 10 ml of 0.02 M NaOH was added and incubated at 25°C for 1 h. The absorbance was measured at 410 nm using an O.R.I. UV4000-Visible spectrophotometer (Germany).

2.3.4 Soil available phosphorous

For measuring soil available phosphorous, 3 g of air-dried soil was mixed with 60 ml 0.5 M $NaHCO_3$ in a 150 ml flask and shaken at 150 rpm for 30 min. The mixture was filtered, and the filtrate was analyzed for soil available phosphorous using an ascorbate-molybdate reagent on a UV Visible spectrophotometer at 880 nm (Arif et al., 2018).

2.3.5 Heavy metals (lead and cadmium)

Soil samples were acid digested with aqua regia (HNO3: HCl; 1:3), and digestate was used for heavy metals (Pb and Cd) analysis through ICP-OES using the method described by O'Shea et al. (2018).

2.4 Statistical analysis

For statistical analysis, Microsoft Excel 2013 was used for the computation of mean and standard deviation (Batool et al., 2015), and the mean values of all treatments were compared through ANOVA and LSD using the "R" program.

2.5 Adsorption isotherm

The Freundlich adsorption isotherm was used to check the efficiency of adsorption at different biochar concentrations, considering the constant ambient temperature on a specified dose, the response was monitored against fluctuating pH, and the modified mechanism of the isotherm calculation was

$$\frac{dy}{dx} = KpH\frac{1}{n}, \tag{9}$$

where dy is the metal removed from the soil, dx is the concentration of the biochar applied, and pH is the pH of the soil corresponding to the removal of the metal from the soil. Taking the log of the equation,

$$log\frac{dy}{dx} = logK + \frac{1}{n}\log pH. \tag{10}$$

log K is the coefficient of the adsorption based on the isotherm, where $1/n$ is the isotherm constant that depends upon the nature of the adsorbent and contaminant at the given temperature. Considering the abovementioned parameters, an intercept plot was plotted for the model fitted values.

TABLE 2 Physicochemical and proximate analyses of *Cannabis sativa* biochar.

Physical and chemical properties	Units	Values[a]> ±S.D.
pH	Nil	9.22 ± 0.2
EC	µS/cm	110.5 ± 0.6
Bulk density	g/cm³	0.163 ± 0.02
Conversion efficiency or yield	%	37.94 ± 0.9
Moisture content	%	5.00 ± 0.1
Ash content	%	3.45 ± 0.15
Volatile content	%	37.91 ± 0.3
Fixed carbon	%	53.64 ± 0.7

[a]Mean of triplicates.

3 Results

3.1 Physicochemical and proximate analysis of biochar

The r physicochemical and proximate analyses of *Cannabis sativa* biochar are presented in Table 2, indicating ash content of around 3.45% with electrical conductivity (EC) of 110.5 µS/cm. The results also indicated a bulk density of 0.163 g/cm³ that can improve soil aeration, and the conversion efficiency was 37.94%. *Cannabis sativa* prepared biochar had a fixed carbon (or residual matter) concentration of 53.64%, while it had a volatile content (mobile matter) of 37.91%.

3.2 Structure and composition analysis of biochar

The surface profile of the prepared biochar indicated through SEM was rough, cracked, and porous. The biochar had sufficient longitudinal pore structures with sizes ranging from 0.70 µm to 3.33 µm. The elemental composition of the prepared biochar was determined using energy dispersive X-ray spectroscopy (EDX) by observing peaks of carbon ©, oxygen (O), potassium (K), calcium (Ca), and chlorine (Cl). The energy dispersive X-ray spectroscopy spectrum of *Cannabis sativa* biochar is presented in Figure 1, while their percentages along with other identified elements are given in Table 3. The carbon percentage was highest (75.3%), followed by oxygen (19.2%), calcium (3.9%), potassium (1.5%), and chlorine (0.08%), which indicated that the biochar was carbonaceous in nature. Apart from the EDX analysis, an inductively coupled plasma optical emission spectrometry (ICP-OES) analysis of *Cannabis sativa* biochar revealed the absence of lead and cadmium in the biochar; however, phosphorus was detected. Fourier transform infrared (FTIR) spectroscopy analysis was performed to investigate the surface functional groups in the prepared biochar presented in Figure 2, while the identified surface functional groups are presented in Table 4.

3.3 Effects of biochar on soil properties and metal immobilization (pot experiment)

In both cases, with the addition of biochar at 1% (BC1) and 5% (BC5), an increase in pH was recorded. Notably, only a slight change in pH was observed in the control treatment over the first 10-day interval (7.71–7.79); however, it remained constant after that throughout the experimental period. In the case of BC1, pH increased from 7.83 to 7.98, showing a 2% increase; whereas, in the case of BC5, pH increased from 7.81 to 7.94, showing a 1.6% increase over the successive 30-day period of incubation. (Figure 3). Considering the EC of the soil, it was found that the addition of BC1 and BC5 caused an increase in EC by 27.08% and 23.51% by the end of incubation.
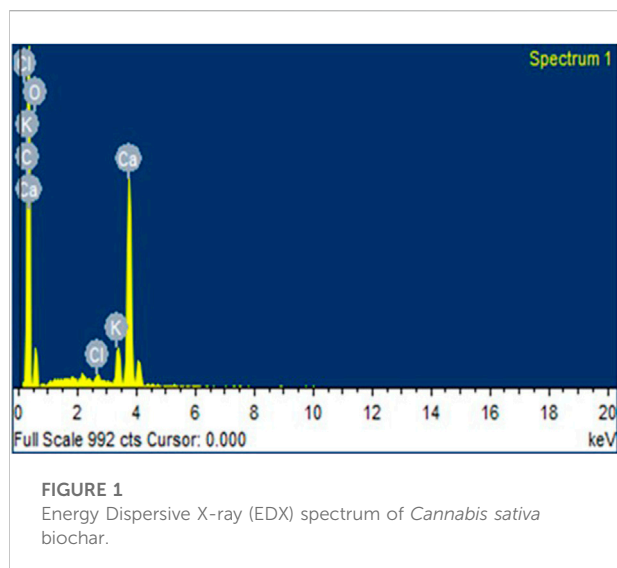
FIGURE 1
Energy Dispersive X-ray (EDX) spectrum of *Cannabis sativa* biochar.

TABLE 3 Elemental composition of *Cannabis sativa* biochar.

Elemental composition	Units	Values[a]> ±S.D.
Carbon[b] (C)	%	75.3 ± 4.6
Oxygen[b] (O)	%	19.2 ± 0.03
Potassium[b] (K)	%	1.5 ± 0.4
Calcium[b] (Ca)	%	3.9 ± 0.6
Chlorine[b] (Cl)	%	0.08 ± 0.01
Phosphorous[c] (p)	ppm	55.26 ± 1.12
Lead[c] (Pb)	ppm	N.D.
Cadmium[c] (Cd)	ppm	N.D.

[a]Mean of triplicate values.
[b]= analyzed through EDX.
[c]= analyzed through ICP-OESN. D. = Not detected.

3.4 Oxidizable organic carbon, total organic carbon, and organic matter

As expected, the addition of 5% biochar considerably increased OC from 1.53 to 2% and TO from 2.04 to 2.66%, whereas OM increased from 3.52 to 4.59% (Figures 4A–C respectively). Meanwhile, the application of biochar at 1% increased OC from 1.51 to 1.74%, TOC increased from 2.01 to 2.32%, and OM increased from 3.5 to 4%. In contrast to control, BC5 exhibited 189.86% increase in OC, 189.13% increase in TOC, and 188.68% increase in OM, while BC1 showed 152.17% increase in OC and TOC and 151.57% increase in OM.

3.5 Soil available nitrogen and phosphorus

Biochar-treated soils presented a notable improvement in soil available nitrogen fraction (Figure 5A). At 1% biochar (w/

w), AN increased from 0.14 ppm to 0.52 ppm, showing a 271.4% increase, whereas the addition of 5% biochar (w/w) increased the AN from 0.16 ppm to 0.6 ppm, indicating a 275% increase. However, as compared to the control, BC1 showed 188.8% increase in AN, while BC5 showed 233.3% increase in AN. SAP increased from 5.28 ppm to 13.56 ppm over 30 days experimental period in BC5, showing a 156.82% increase, whereas SAP increased from 5.23 ppm to 10.08 ppm in BC1 treatment over the experimental time frame, indicating a 92.73% increase in concentration (Figure 6). As compared to the control, BC1 showed a 50% increase in SAP, whereas a 101.79% improvement was observed for BC5.

3.6 Heavy metals

Concentrations of lead (Pb) in control, BC1, and BC5 are presented in Figure 6A. During the experimental period, Pb concentration in control was observed to increase with time ranging from 3.97 ppm to 5.64 ppm, indicating a 42.07% increase. However, comparatively, both biochar treatments showed reductions in Pb concentrations. In BC1, lead concentration (ppm) the lead concentration decreased as 3.91 > 3.57 > 3.26 > 3.06. In comparison with the control, BC1 showed a reduction in Pb concentration by 0.06 (1.51%), 0.75 (17.36%), 1.66 (33.74%), and 2.58 (45.74%) ppm at 0- , 10-, 20-, and 30-day intervals, respectively. In BC5 treatment, lead concentration (ppm) decreased over the entire time of 30 days in the following order: 3.87 > 3.63 > 3.58 > 3.43, whereas Pb concentration decreased by 0.24 ppm (6.2%), 0.05 ppm (1.38%), and 0.15 ppm (4.19%) during the first, second, and third intervals, respectively. In comparison with the control, BC5 showed a reduction in Pb concentration by 0.1 (2.52%), 0.69 (15.97%), 1.34 (27.24%), and 2.21 (39.18%) ppm at 0- , 10-, 20-, and 30-day intervals, respectively.

Similarly, both biochar amendments effectively reduced the Cd concentration in the soil as compared to the control (Figure 6B). Over the 1-month experimental duration, Cd concentration in control was observed to increase with time ranging from 0.55 ppm to 0.76 ppm, showing a 38.18% increase in concentration. However, in BC1, cadmium concentration (ppm) decreased in the following order: 0.52 > 0.46 > 0.38 > 0.33. Cadmium concentrations decreased by 0.06 ppm (11.54%), 0.08 ppm (17.39%), and 0.05 ppm (13.16%) during the first, second, and third intervals, respectively. As compared to control, BC1 showed a reduction in Cd concentration by 0.03 ppm (5.45%), 0.15 ppm (24.59%), 0.31 ppm (44.93%), and 0.43 ppm (56.58%) at 0-, 10-, 20-, and 30-day intervals, respectively. In case of BC5, Cd concentration (ppm) decreased over the entire 30 days pot experiment in the following order: 0.54 > 0.50 > 0.47 > 0.42. Cadmium
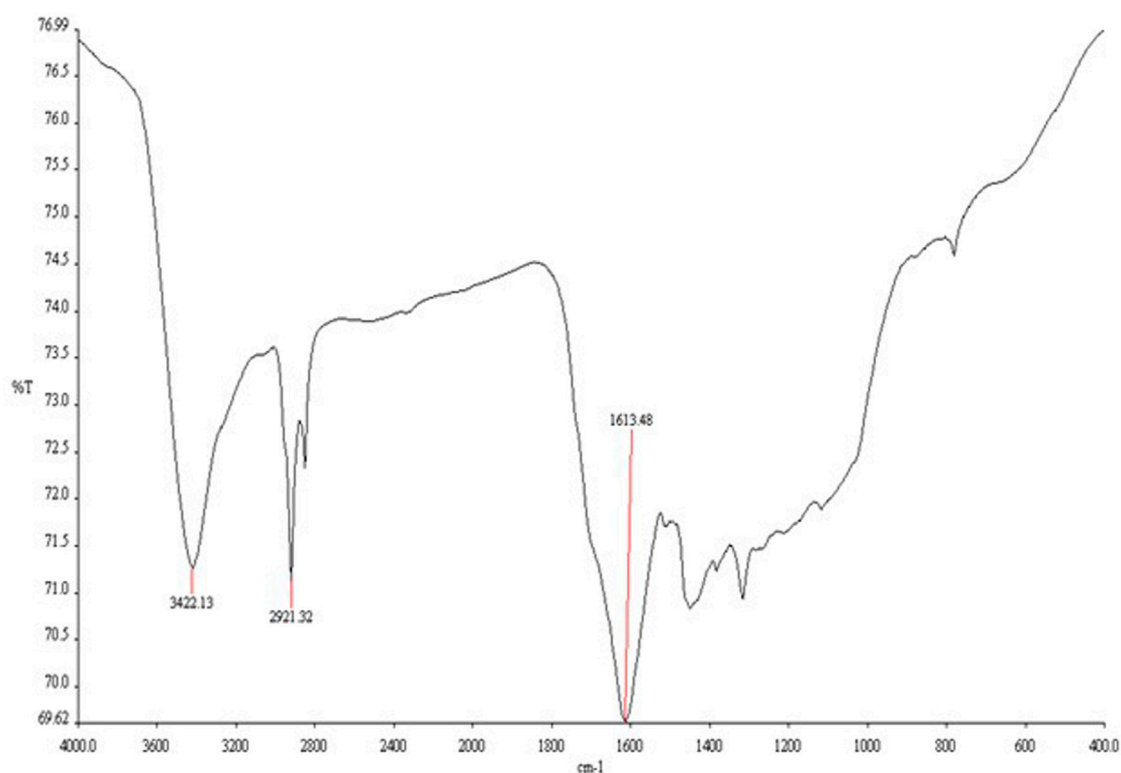
FIGURE 2
FTIR spectrum of *Cannabis sativa* biochar.

concentration decreased by 0.04 ppm (7.41%), 0.03 ppm (6%), and 0.05 ppm (10.64%) at the first, second, and third intervals, respectively. In comparison with the control, BC5 also showed a reduction in Cd concentration by 0.01 ppm (1.82%), 0.11 ppm (18.03%), 0.22 ppm (31.88%), and 0.29 ppm (38.16%) at 0-, 10-, 20-t, and 30- day, respectively.

3.7 Adsorption isotherms

The adsorption isotherms were obtained for a constant ambient temperature of 24°C (±2) and concentration of the biochar applied, considering the pH as fluctuating and controlling factor. It was found that at 1% biochar application, the intercept value for cadmium was negative, indicating the low adsorption at the lower pH of cadmium. Overall, the intercept values for lead and cadmium were 1.9006 and 0.012, respectively, keeping the constant concentration of biochar at1%. Interestingly, at a 5% biochar application rate, the intercept values were 1.02 and 0.052 for lead and cadmium, respectively. The linear fitted slope indicated a constant distribution of adsorbent over the pH change (Figure 7).
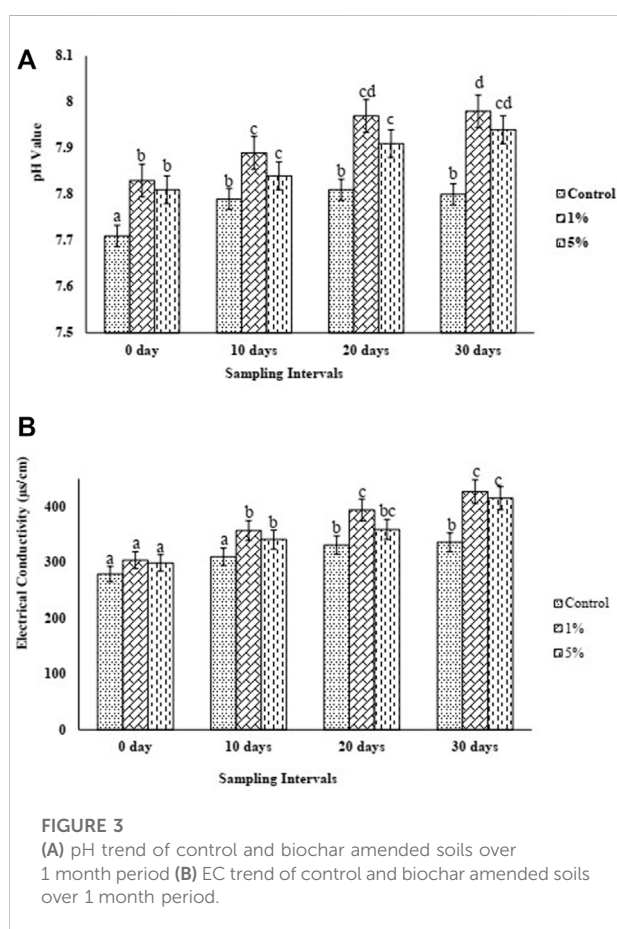
4 Discussion

4.1 Physicochemical and proximate analysis of biochar

Cannabis sativa (industrial hemp) is an invasive plant species found abundantly in Islamabad (Khan et al., 2010). The plant biomass pyrolyzed at 450°C showed a high pH value of 9.22, indicating its alkaline nature. These findings were in line with previous studies stating that an increase in temperature results in a higher pH of biochar (Al-Wabel et al., 2017; Poo et al., 2018). A temperature range of 200°C to 300°C causes cellulosic materials to decompose, resulting in alcoholic and phenolic substances (-OH containing substances) that impart alkalinity to biochar. Moreover, at temperatures above 300°C, alkaline minerals begin to disengage from the organic matrix, resulting in increased pH (Poo et al., 2018; Waqas et al., 2018). Identical to *Cannabis sativa* biochar, alkaline biochar was also obtained as a result of using woody materials, *Lantana camara* and *Cladophora patentiramea* (algal specie) (Bird et al., 2011; Qadeer et al., 2014; Rees et al., 2014). Biochar derived from *Conocarpus* tree species waste at 400°C ± 10°C was also reported to have a pH of 9.85 (Al-Wabel et al., 2015).

TABLE 4 Surface functional groups of *Cannabis sativa* biochar.

Wavenumber (cm⁻¹)	Functional group identified
3,422.13	O-H and–H stretching (alcohols, phenols, and organic acids)
2,921.32	Aliphatic C-H stretching and N-H stretching (amine)
1,613.48	Conjugated C=C and C=O (aromatic structures)
1,430.98	C=O stretching (carbonyl group) and N-H stretching (amine)
1,312.3	C-O stretching (esters and ethers) and O-H deformed vibrations (alcohols and phenols)

FIGURE 3
(A) pH trend of control and biochar amended soils over 1 month period **(B)** EC trend of control and biochar amended soils over 1 month period.

The ash content was subjected to pyrolysis temperature because an increase in temperature resulted in higher ash content since the minerals and combustion residues of organic matter become concentrated at high temperatures (Ahmad et al., 2012). High ash content in biochar is generally undesirable at higher temperatures, and metal volatilization can result in serious issues of air pollution. Moreover, it also hampers the
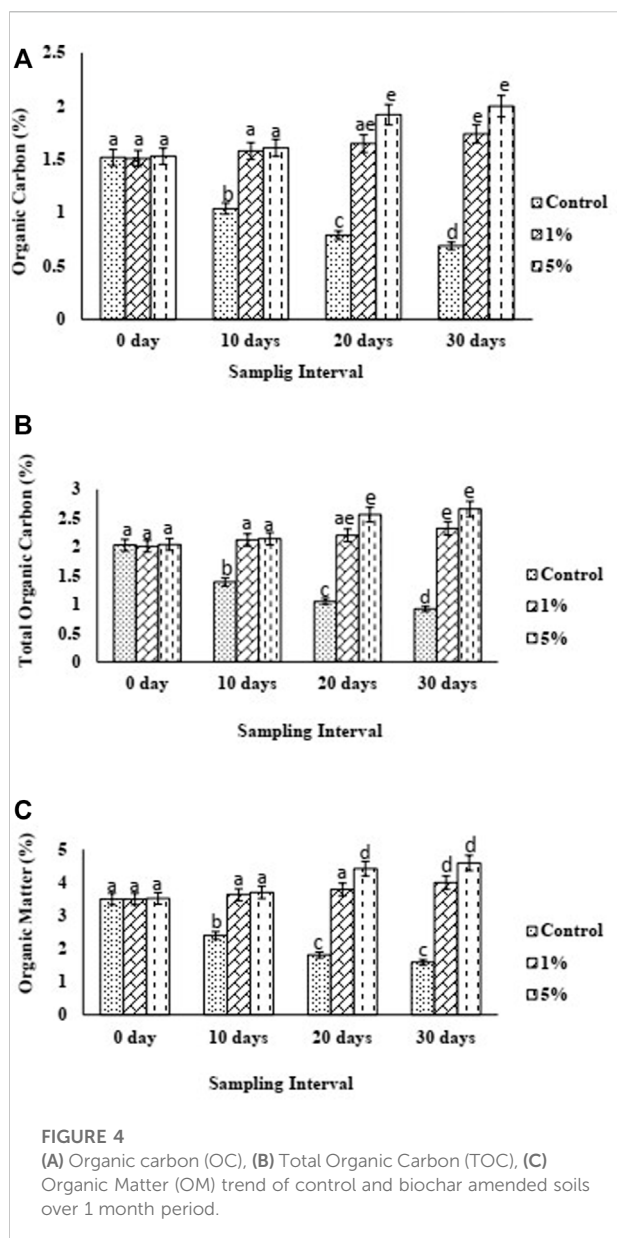
development of aromatic carbon structures (Enders et al., 2012). Electrical conductivity is based on the ash content of biochar, such that higher ash content can impart a higher EC of biochar (Ahmad et al., 2017). Most of the volatiles are removed because of pyrolysis, leaving behind exchangeable cations such as Ca^{+2} and Na^+, which concentrate and, thereby, increase the pH and EC of biochar (Waqas et al., 2018). Ahmad et al. (2017) reported an EC of 150 μS/cm for biochar produced at 300°C from peanut shells. A very low EC of 0.09 μS/cm was obtained by Pourret and Houben (2018) for a sewage sludge biochar prepared at 500°C.

Low bulk density is desirable for plant growth, with the ideal bulk density being <1.6 g/cm³. The addition of biochar lowers the bulk density of the soil and, thus, improves soil aeration (Reverchon et al., 2014; Tan et al., 2018). Low bulk density can enhance soil quality as it aerates the soil, making it more effective for holding water, which, in turn, promotes better growth and development of the plant root system (Hossain et al., 2010). As bulk density is inversely proportional to organic matter and porosity (Khater, 2015; Juma et al., 2018), the obtained low bulk density of *Cannabis sativa* biochar (0.163 g/cm3) indicated high porosity and organic matter in biochar. This porous nature is further confirmed by SEM of the biochar indicating up to 3.33 μm pore length (Figure 8).

The obtained conversion efficiency of 37.94% is more than usually expected (~35%) during slow pyrolysis (Sohi et al., 2010; Ahmad et al., 2014). Since the conversion efficiency of biochar is inversely proportional to the temperature, thus, the current noticeable conversion efficiency can be explained by the low pyrolysis temperature (Sohi et al., 2010; Hernandez-Mena et al., 2014; Poo et al., 2018). The maximum biomass loss occurs when the hemicelluloses degrade at a temperature range of 250°C to 350°C. Cellulosic components of the biomass begin to decompose at temperatures ranging from 325°C to 400°C, while lignin structures start to degrade at temperatures ranging from 300°C to 550°C (Poo et al., 2018). This indicates that most of the compounds retained in the biomass could be related to lignin-related compounds, followed by cellulosic compounds. The same can be related to the functional group analysis of the biochar that indicated aliphatic and aromatic stretching of the biochar (Table 4). However, in addition to pyrolysis temperature, the type of feedstock utilized for biochar production has an impact on biochar properties, including its yield (Uchimiya et al., 2010; Spokas et al., 2012; Ahmad et al., 2017; Sandhu et al., 2017; Grutzmacher et al., 2018). It was also found that temperatures higher than 450°C can lead to the degradation of lignin (Li Y. et al., 2021). Therefore, it is critical to control the process conditions like temperature and residence time to get an efficient biochar product (Ahmad et al., 2017).

Fixed carbon is a representative of the completely carbonized organic matter within the biochar, presenting its stability in the soil as it is subject to slow microbial and

FIGURE 4
(A) Organic carbon (OC), **(B)** Total Organic Carbon (TOC), **(C)** Organic Matter (OM) trend of control and biochar amended soils over 1 month period.
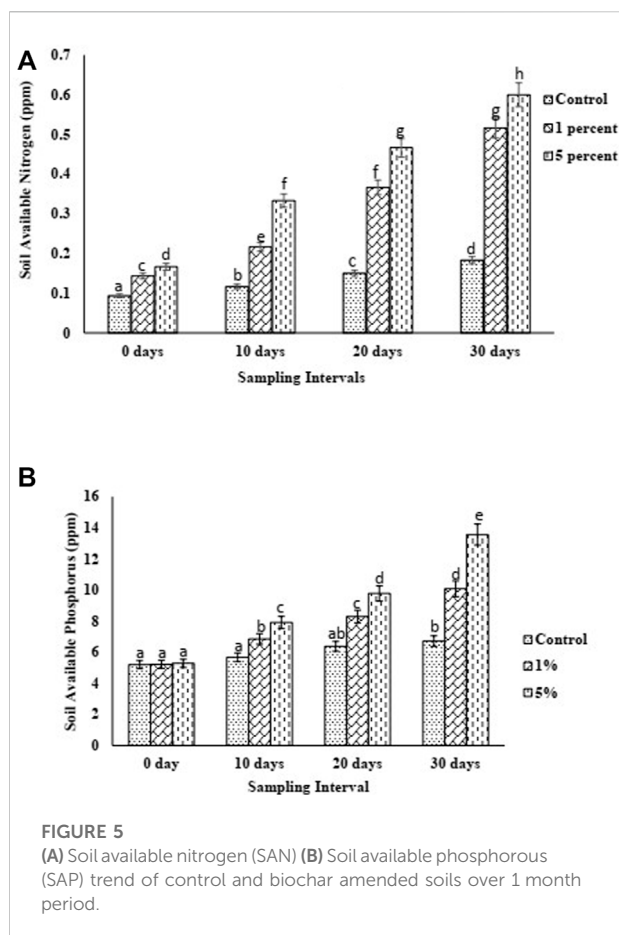
chemical decomposition, whereas volatile content provides a carbon source for the soil microflora and improves soil health (Ahmad et al., 2014; Juraszek and Piasecka, 2020; Medyńska-Juraszek and Ćwieląg-Piasecka, 2020). Volatile content is generally believed to reflect the stability of biochar, such that higher volatile content indicates low stability and lower volatile content points to the high stability of biochar (Waqas et al., 2018). This implies that *Cannabis sativa* biochar is more labile and, therefore, it contributes to enhancing the soil organic pool and plays an effective role in improving soil fertility. The higher fixed carbon, as compared to volatile carbon, can be recognized as a sustainable carbon pool in

the soil. This is in contradiction to some previous studies where it was found that biochar with low fixed carbon can serve as a better source for increasing soil nutrient pool (Chaturvedi et al., 2021). The contradictory results can be explained by the fact that fixed carbon may not be readily available for increasing the soil carbon content. But it is a consistent source of slow carbon release in the soil. In a previous study, biochar was prepared from agricultural green waste at 450°C and reported a fixed carbon content of 14.1% and a volatile content of 7.6% (Waqas et al., 2018), providing more of a stable biochar, effective for carbon sequestration and mitigating climate change. Such differences in the physicochemical properties of biochar produced at the same pyrolysis temperature, i.e., 450°C, can be explained by the usage of different feedstocks and residence times (Sandhu et al., 2017; Grutzmacher et al., 2018). The volatile content of biochar is also indicative of nitrogen availability and, hence, plant growth (Enders et al., 2012).

4.2 Structure and composition analysis of biochar

Low-temperature pyrolysis (450°C) causes the thermal breakdown of hemicelluloses and cellulosic plant materials, thereby giving rise to large pore spaces that can serve as a habitat for soil microflora, which ultimately improves soil health (Pattnaik et al., 2018). This further explains the low bulk density of the prepared biochar. Hernandez-Mena et al. (2014) suggested that the formation of large pores is due to the vascular bundles of the raw plant material. Moreover, the longitudinal pore shape is the result of the distortion of the original porous structure of the plant during pyrolysis (Hardie et al., 2014), which helps vapors that were produced during pyrolysis to escape (Hernandez-Mena et al., 2014). This porous structure of biochar helps in retaining water and nutrients that can be beneficial for soil quality and soil microflora (Hamdani et al., 2017).

The elemental composition of biochar was greatly influenced by the composition of the feedstock from which it was derived and the pyrolysis temperature during its production (Enders et al., 2012). A previous study also reported carbon and oxygen percentages of 77.81 and 8.76%, respectively, for biochar produced at 450°C (Waqas et al., 2018). Biochar rich in carbon can play an important role in carbon sequestration and contaminant adsorption from soil (Hernandez-Mena et al., 2014). Surface functional groups play an important role in binding the metal cations; hence, heavy metals and other nutrient cations such as K^+ and Mg^{+2} remain adsorbed to the biochar surface. This ensures heavy metal immobilization and reduced nutrient leaching in soil, both of which are desirable

FIGURE 5
(A) Soil available nitrogen (SAN) **(B)** Soil available phosphorous (SAP) trend of control and biochar amended soils over 1 month period.

4.3 Effects of biochar on soil properties and metal immobilization

The addition of biochar caused an increase in the pH that can be attributed to the alkalinity of biochar. Higher pyrolysis temperatures generally yield high pH biochar with more basic surface functional groups and reduced acidic groups, promoting an overall liming effect (Al-Wabel et al., 2017). Biochar was reported to carry basic cations such as Ca$^+$, Mg$^+$, Na$^+$, and K$^+$ that convert into hydroxides, oxides, and carbonates, resulting in increased alkalinity of the soil and, hence, its pH (Mehmood et al., 2018). Biochars were generally characterized by having a porous nature and large surface area. These attributes of biochar were the main reason for imparting a high cation exchange capacity (CEC) to biochar, which, in turn, resulted in higher soil pH. About 68% of the changes in soil pH following biochar addition was attributable to the property of high cation exchange capacity (Nigussie et al., 2012). Similarly, the increase of EC in the control can be attributed to native soil organic matter mineralization (Al-Wabel et al., 2017). The addition of biochar at BC1 and BC5 increased EC due to the ash inclusions that were present within the biochar, which contains soluble salts (Figure 4B). These salts imparted a higher soil EC when biochar was decomposed or oxidized (Al-Wabel et al., 2017; Ghorbani and Amirahmadi, 2018). In addition, hydrophobic compounds also leach from the biochar to alter the soil EC (Loper et al., 2010). Furthermore, increased soil EC can be linked with the ionic content of biochar (Ahmad et al., 2017). Previously, consistent findings were reported by Mehmood et al. (2018) over a period of 60 days. Similarly, many other researchers have reported an increase in soil pH (Hossain et al., 2010; Qadeer et al., 2014; Rees et al., 2014; Bashir et al., 2018; Rizwan et al., 2018) and soil EC as compared to the control on the addition of biochar to soil (Hossain et al., 2010; Rizwan et al., 2018).

4.4 Oxidizable organic carbon, total organic carbon, and organic matter

The application of biochar primarily increased the organic matter, which improved soil organic carbon (Hamdani et al., 2017). The results of the current study are compatible with previous work and showed a rise in all types of carbon content (Qadeer et al., 2014; Manore et al., 2021). Oxidizable organic carbon, total organic carbon, and organic matter are interconnected, which implies that a change in one induces a change in the others. As a result, the application of biochar at 1% and 5% can be justified by the fact that biochar produced at low pyrolysis temperatures had a substantial volatile carbon content, (which can be characterized by high volatile carbon in the current study) which, being mobile in

scenarios (Paz-Ferreiro et al., 2014; Bashir et al., 2018). However, this also comes with a critical point of fixing soil micronutrients inside the soil (Mikula et al., 2020).
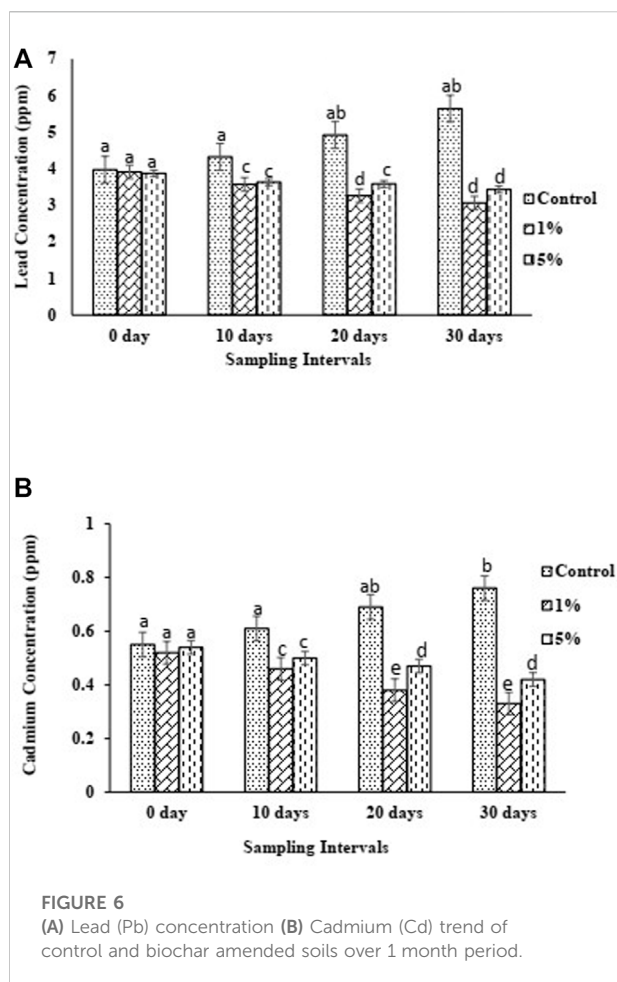
The band at 3,422.13 cm-1 corresponded to O-H and H-bonded stretching of phenols and alcohols along with organic acids (Poo et al., 2018; Pourret and Houben, 2018). These may have appeared due to moisture within the samples (Chia et al., 2012). A peak at 2,921.32 cm-1 represented the aliphatic C-H stretching, indicating the presence of hemicellulose and cellulose and N-H stretching in the carbonyl group (Begum et al., 2016; Waqas et al., 2018). The peak observed at 1,613.48 cm-1 indicated the C=C and C=O bond in aromatic structures, imparting aromaticity to the biochar (Ahmad et al., 2012; Begum et al., 2016; Çaglar et al., 2018). The band at 1,430.98 cm-1 presented the C=O and N-H stretching in carbonyl and amine functional groups, respectively (Pattnaik et al., 2018), whereas the peak at 1,312.32 cm-1 indicated the presence of hemicelluloses through C-O stretching in esters and ethers (Armynah et al., 2018) and deformed O-H vibrations of alcohols and phenols (Angın, 2013).

FIGURE 6
(A) Lead (Pb) concentration **(B)** Cadmium (Cd) trend of control and biochar amended soils over 1 month period.
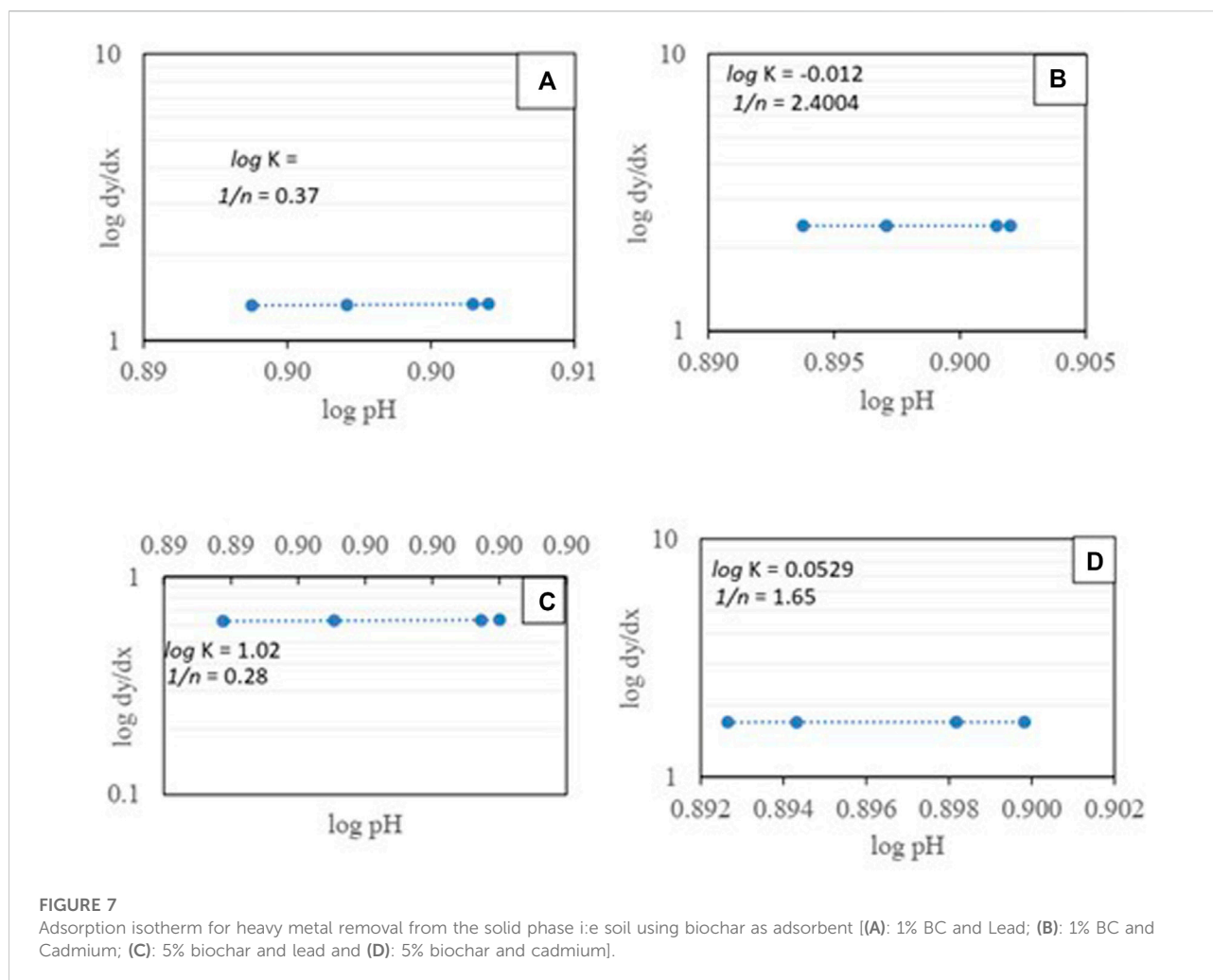
because it enhanced the soil microbial community (Ahmad et al., 2014; Luo et al., 2018). Previously, many studies have documented that biochar application increased soil organic carbon (Bashir et al., 2018; Tan et al., 2018; Zheng et al., 2018).

4.5 Soil available nitrogen and phosphorus

Biochar can provide nutrients to the soil directly because it contains nitrogen, phosphorous, potassium, magnesium, and calcium (Nelson et al., 2011). Similar results of increased AN in response to biochar addition were reported by other studies (Ghorbani and Amirahmadi, 2018; Tan et al., 2018; Zheng et al., 2018). Progressive mineralization of biochar in soil releases inherent nutrients into the soil (Jain et al., 2018; Zheng et al., 2018). Moreover, enhanced pH due to alkaline minerals in biochar promotes the formation of NH_3 (Liu et al., 2018), which takes part in the nitrification process because biochar addition stimulates the activity of nitrifying bacteria (Song et al., 2014), which increases AN. The positive priming effect of biochar, i.e., accelerating the decomposition of already present organic matter in the soil, can also be the cause of enhanced AN (Ahmad et al., 2014). In addition to increasing AN content, biochar can effectively adsorb nitrate and ammonium ions through surface functional groups; mainly the hydroxyl and carboxyl groups, thereby retaining their availability in soil over a longer period (Tan et al., 2018; Zheng et al., 2018). Phosphorous is a vital component of plant growth, and its availability can be affected by biochar (Reverchon et al., 2014). Increased SAP could be the result of the direct addition of biochar itself to the soil because of its inherent available nutrients, such as phosphorous and potassium (Qadeer et al., 2014; Zheng et al., 2018). The increase in SAP over the experimental period supports the finding that with an increase in biochar application rates, SAP was increased. Gradual increment in SAP over the 1-month period can also be attributed to the phosphorous compounds present in the ash content of biochar, as reported previously (Chen et al., 2019).
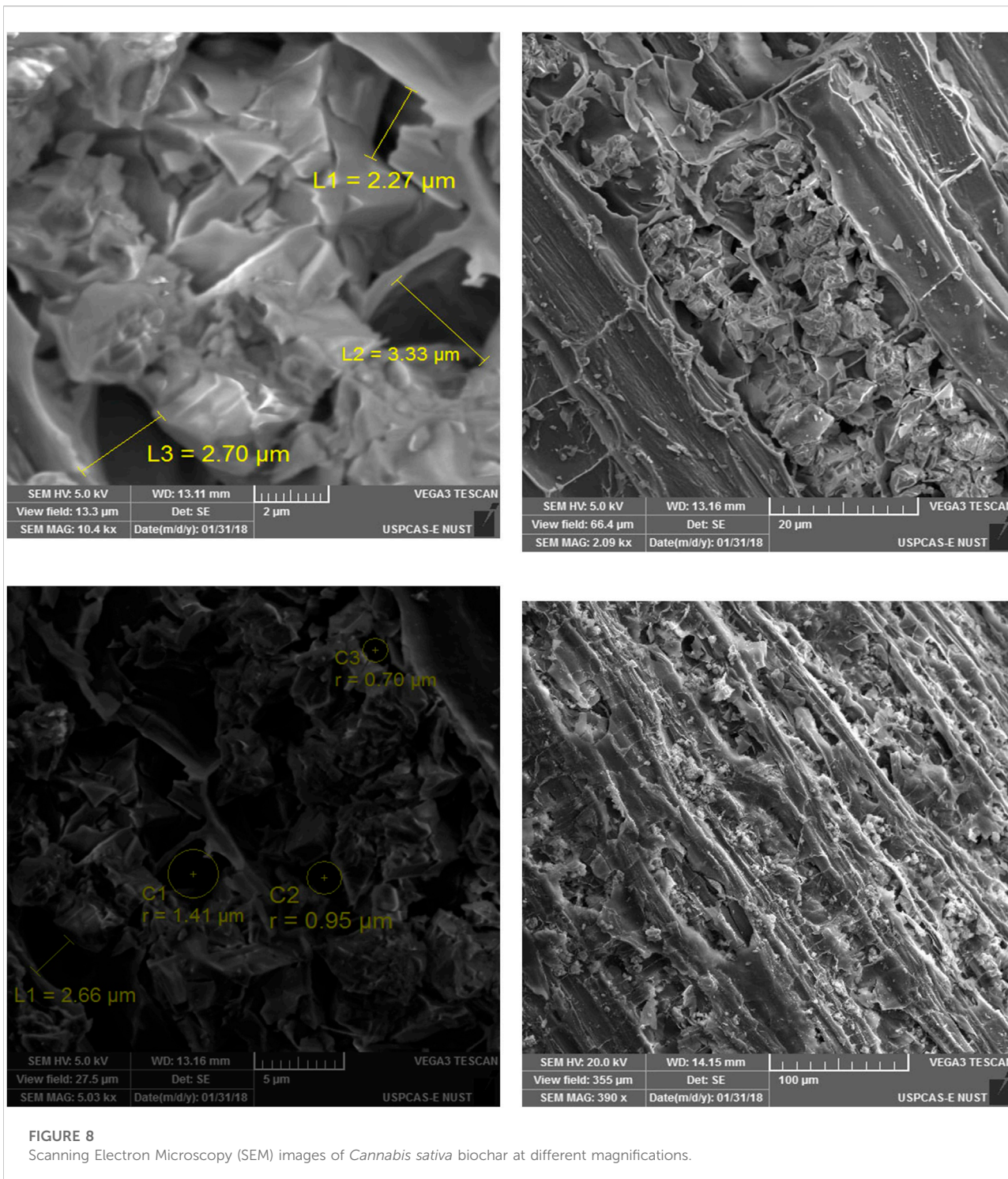
4.6 Heavy metals

The use of biochar to stabilize heavy metals was a proven approach, and it was considered a low-cost and efficient solution to the heavy metal contamination problem (Poo et al., 2018; Lian et al., 2020). The decrease in metal concentration was observed in the current work. Park et al. (2011) reported similar results of reduced soil Pb and Cd concentrations upon applying chicken manure and green waste–derived biochar. Many other studies also reported reduced Cd concentrations in soils after biochar application (Abbas et al., 2017a; Rizwan et al., 2018; Van Poucke et al., 2018). Additionally, Fellet et al. (2011), Park et al. (2013), Lu et al. (2017), and Lian et al. (2020) also observed a reduction in heavy metals (Pb and Cd) concentration in soils treated with biochar. Biochar treatment of 1% (w/w) proved to be more effective in immobilizing lead as compared to the 5% biochar

nature, replenishes soil carbon and serves as a source of energy for soil micro flora (Jindo et al., 2014). Therefore, since the fraction of volatile carbon is homogenous in biochar, increasing the concentration of biochar is a factor of high organic matter and oxidizable carbon in the soil. Biochar, being highly carbonaceous in nature, was mineralized by soil microbes over time, and this led to a 0.3–0.8% loss of total assimilated carbon from biochar within almost initial 2 months of biochar application. Biochar contains a labile carbon fraction that can leach easily and replenish soil carbon content, allowing soil biota to flourish and improve soil fertility. The decrease in organic carbon in control treatment may be attributed to the progressive decomposition of the already present organic matter in the soil (Al-Wabel et al., 2017). In addition, biochar application increased soil pH levels, causing the release of labile carbon fraction from biochar into the soil and, thus, increasing organic carbon lability (Li et al., 2018). Increased pH also induces chemical hydrolysis of already present soil organic matter (Ahmad et al., 2014), thereby, increasing the available carbon content in the soil. In addition, native soil carbon readily decomposed because of applying biochar (positive priming effect)

FIGURE 7
Adsorption isotherm for heavy metal removal from the solid phase i:e soil using biochar as adsorbent [(A): 1% BC and Lead; (B): 1% BC and Cadmium; (C): 5% biochar and lead and (D): 5% biochar and cadmium].

treatment (w/w), but overall, both biochar amendments were successful compared to the control in reducing the soil lead concentrations. In addition to the biodegradable fraction, much of the biochar was composed of the recalcitrant carbon fraction that ensures its sustenance in the soil for thousands of years. Furthermore, it is renowned for its ability to adsorb heavy metals, rendering them immobile (Al-Wabel et al., 2017; Shen et al., 2018; Lian et al., 2020; Tu et al., 2020). This can be achieved either through the formation of surface complexes (with surface functional groups) and/or precipitates (in the form of carbonates and phosphates) or through electrostatic attraction (Shen et al., 2018). Wang and Liu (2017) also reported the phenomenon of cation exchange (in which biochar-associated nutrient cations such as Na^+, Mg^{+2}, and Ca^{+2} were exchanged with soil heavy metal cations such as Pb^{+2} and Cd^{+2}) and physical sorption to be involved in the immobilization of heavy metals. As for the current study, the reduction in the heavy metals (Pb and Cd) concentration could be attributed to the formation of Pb and Cd carbonates and phosphates (Rees et al., 2014; Mehmood et al., 2018). The ash content of biochar was accompanied by many different compounds, including phosphates, carbonates, and sulphates. These compounds play an important role in stabilizing the heavy metal cations in soil by precipitation of these contaminants (Paz-Ferreiro et al., 2014) in the form of insoluble metal carbonates (Al-Wabel et al., 2017). Moreover, increased pH due to the biochar addition could also be the cause of metal immobilization facilitated by hydrolysis. Adsorption is also an explanation for the metal stabilization scenario because biochar, being negatively charged, attracts the positively charged heavy metal cations (Mehmood et al., 2018). Various functional groups identified on biochar surface through SEM analysis also support the possibility of surface complexation of metals with the organic functional groups, rendering the heavy metals immobile in the form of organo-metal complexes (Al-Wabel et al., 2017; Mehmood et al., 2018; Qi et al., 2018). It was also found that the addition of biochar has a significant effect in increasing the soil microbial community that can aid in the stabilization and passivation of the metals through the inorganic ion transport mechanism (Lan et al., 2021).

FIGURE 8
Scanning Electron Microscopy (SEM) images of *Cannabis sativa* biochar at different magnifications.

The current study sheds light on the usage of organic value-added products to enhance soil fertility in addition to being an environmentally benign choice for remediation. Additionally, it offers a fresh perspective because biochar may be combined with various substrates and nanomaterials to increase its effectiveness and longevity in a system. In other words, biochar can be used as a growth medium for advantageous rhizobacteria, which, in turn, promote agriculture and soil health. It provides multiple ways to improve agriculture and full the food demand in a sustainable way.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material; further inquiries can be directed to the corresponding author.

Authors contribution

AS and QM contributed to the conception and design of the study. ZA and Waqar-Un-Nisa executed the laboratory work and prepared the first draft of the manuscript. AS and SQ refined sections of the manuscript. LR provided a brief review and performed proofreading. All authors contributed to manuscript revision, read, and approved the submitted version.

Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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