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Abstract

By expanding the surface area and/or by other chemical reactions, soil additives such as biochar help retain nutrients in the soil. n this work, the effects of biochar on the adsorption and desorption of heavy metals and soil elements necessary for plant growth were investigated. To illustrate the adsorption of nutrients and heavy metals from solution on biochar, the Freundlich isotherm was employed. The rise in mineral nutrients, pH, and EC was linked to an increase in CEC with warmth. Because of its high CEC, biochar improves soil health and increases plant nutrient availability, which can boost agricultural yield when applied to the soil. In manure + biochar at 2.5 + 7.5 t/ ha application rate the NH₄⁺-N adsorption capacity was minimum in T_7 (15.9 and 117.66) followed by T_4 (17.6 and 130.24), T_{13} (18.7 and 138.38) and maximum in T_{10} (20.1 and 148.74) at 25 and 200 mg kg⁻¹ level of added NH₄⁺-N, respectively than control T_1 (10.3 and 75.3). An increase in the rate of biochar application led to a favourable effect by increasing the NO3–N adsorption capability. The effect on P adsorption was more with biochar than manures. In manure + biochar at 2.5 + 7.5 t/ha application rate the Pb adsorption capacity was minimum in T_7 (4.46 and 30.77) followed by T_{10} (4.71 and 32.49), T_{13} (5.16 and 35.60) and maximum in T_4 (5.48 and 37.81) at 10 and 100 mg kg⁻¹ level of added Pb, respectively than control T₁ (1.86 and 12.83). Goat manure, FYM, vermicompost, and poultry manure had the greatest effects on desorption. The desorption of all heavy metals Cd, Pb, Zn, and As decreased as the rate of biochar application increased. Based on excess nutrients and heavy metals, this study supports the use of biochar to mitigate environmental concerns.

Keywords Biochar, Organic manure, Adsorption, Desorption, Heavy metal, Ammonia nitrogen, Nitrate nitrogen

Introduction

The incorporation of biochar into soil can modify its characteristics, such as its capacity to absorb and break down various substances. By enhancing the soil's ability to hold nutrients and water, biochar may be used to improve soil fertility in addition to acting as a carbon

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¹ICAR Research Complex for NEH Region, Sikkim Centre, Tadong, Gangok 737102, Sikkim, India sink (Wang et al. 2018). Because of its high surface area, low bulk density, high ratio of micropores to macropores (Yingjie et al. 2023), and high CEC, it is also an excellent adsorbent of nutrients and chemicals. Although organic matter plays a significant role in the process by which nutrients are absorbed by soil, the impact of organic matter on soil nutrient adsorption is complex (Hung et al. 2018). In order to manage agricultural soils, it is essential to comprehend the chemical alterations that take place in soils modified with biochar (Karim et al. 2017). The greater water retention of biochar, which prevents the leaching of mobile nutrients, the faster growth rate



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of microorganisms, and changes to the soil's N cycle process have all been linked to the retention of nutrients in the soil (Kavitha et al. 2018). Because of their high cation exchange capacity, large surface area, and acidic surface groups, biochars pyrolyzed products made from crop residues are applied to soil to enrich the recalcitrant portion of the soil organic carbon (Sixu et al. 2023, Das et al. 2020b). The rate of biochar application, the type of biochar used, the features of the soil, and the environmental factors all affect how much N is leached when using biochar. Through modifications to soil porosity, pore connectivity, pore shape, and tortuosity of the conducting soil pores, biochar may have an impact on K levels (Das et al. 2023b, c, d, e). Other physico-chemical properties like high ion-exchange capacity can also have an impact on a number of processes in the soil N cycle related to improved soil fertility (Kavitha et al. 2018; Luo et al. 2023; Liu et al. 2023) When biochar was produced at high temperatures (>600 °C), the inhibition of nitrification and consequently the decreased nitrate generation were discovered to be the mechanisms of decreased nitrate leaching (Kang et al. 2022; Wang et al. 2022; Das et al. 2023b, c, d, e).

The adsorption of NO₃⁻ on the anion exchange surface of biochar was shown to be particularly important (Zhang et al. 2017; Tan et al. 2018; Waqas et al. 2018; Das et al. 2023b, c, d, e). When biochar is added to soil, it enhances the soil's physical characteristics, boosts the cation exchange capacity (CEC), and eventually improves nutrient retention (Das et al. 2022; Singh et al. 2015). We don't fully understand how biochar amendments affect soil nutrients. The impact of biochar and organic manure on the leaching of nutrients has not been adequately demonstrated by research. Keeping the importance of soil nutrients leaching and heavy metal pollution our current study was conducted to investigate the adsorption and desorption of different soil nutrients as well as heavy metal in soil utilizing biomass derived biochar and organic manure as an emerging new generation adsorbent. We have evaluated the adsorption potential of NH₄⁺-N, NO₃⁻-N, phosphorus (P), potassium (K), lead (Pb), Cadmium (Cd), Zinc (Zn) and Arsenic (As). We have also evaluated the desorption potential of the above-mentioned minerals and heavy metals.

Materials and methods

Experimental details

The experimental set up was located at 1350 m above the mean sea level (msl) and represents sub-tropical mid hill location of Sikkim and lies at 27°20'N latitude and 88°37'E longitude. The experimental site was sandy loam to clay loam in texture, acidic in pH and high in organic matter content. Four different types of organic manure viz. Farmyard manure (FYM), poultry manure (P_0M), goat manure (GM), vermicompost (VM) and biochar viz. Maize stalk (MS) were used. Total number of treatments was 13 and the treatment was distributed in completely randomized block design (CRD experimental design) with three replications per treatment along with control. The experimental area received an annual rainfall of more than 3000 mm. Rainfall was well distributed during the months of May to September. June and July are the wettest month during that year. The hottest months were July and August; and coldest are December and January. The reagents used for soil analysis were of analytical grade (AR) and were purchased from different repute company in India. The glass wares used in different experiment in this study were of Borosil made. The treatment details of the experiment were T_1 : control; T_2 : FYM 7.5%+biochar 2.5%; T₃: FYM 5% +biochar 5%; T₄: FYM 2.5%+biochar 7.5%; T₅: P₀M 7.5%+biochar 2.5%; T₆: P₀M 5%+biochar 5%; T₇: P_oM 2.5%+biochar 7.5%; T₈: GM 7.5%+biochar 2.5%; T₉: GM 5% +biochar 5%; T₁₀: GM 2.5%+biochar 7.5%; T₁₁: VC 7.5%+biochar 2.5%; T₁₂: VC 5%+biochar 5%; T₁₃: VC 2.5%+biochar 7.5%.

Biomass collection and biochar preparation

Maize stalk biomass was collected from the ICAR-Sikkim centre research farm from previous crop harvesting. The biomass was shredded to pieces of ≤ 6 inch and oven dried at 70 °C followed by pyrolysis into biochar production unit. Charring of all the biomass (moisture level 5%) was carried out in a portable charring kiln (28 inch length ×10 inch diameter) developed by ICAR-Sikkim centre to keep the process quick, low cost and simple. Biomass was inserted into kiln, combusted at 400, 500 and 600°C (heating rate 10 °C min⁻¹ and holding temperature 4.0 h) and the temperature was maintained by electrically operated manual switch connected to the kiln. After preparing the biochar were collected with shovel/scoop, dried at 100 °C (24 h), pulverized to fine powder, sieved through 0.2 mm and used for further physico-chemical characterization.

SEM, TEM and FT-IR analysis of biochar

Using the scanning electron microscopy (SEM) instrument (ZEISS 1550VP field emission SEM) the surface morphology of all the biochar was determined having operating condition 15.0 kV accelerating potential (P.C. 30 HV). We have utilized a secondary electron detector (SED) with 8 mm WD to generate the topographic SEM image. The transmission electron microscopy (TEM) analysis was carried out using 2 mg biochar mixed with 20 mL of 1-methyl-2-pyrrolidone solvent and sonication at 53 kHz (30 min) followed by centrifugation at 1000 rpm (1 h). Then the C-film coated Cu-grid was generated in a vacuum evaporator (JEOL.JEE-420). The supernatant was dropped onto the C-film coated grid. TEM analysis was done with electron microscope (model no- JEM-1011, JEOL) to record various black dots at at 200 kV and the digital images were processed. The fourier-transform infrared spectroscopy (FT-IR) analysis of biochar was done with a Bruker ALPHA FT-IR spectrometer over $500-4000 \text{ cm}^{-1}$ wavenumbers for identification of different biochars' functional groups. The biochar samples (0.1%) were mixed and ground with solid KBr in order to prepare KBr-pellet thin films for analysis with FT-IR.

Adsorption-desorption study

Using batch equilibration method, the adsorption isotherms for N, P, K and heavy metal in soils were obtained. To determine equilibration time, 10 g soil was taken in a series of centrifuge tubes along with 25 ml of known concentration of NH₄NO₃, KH₂PO₄ and heavy metal solution and kept shaking for different time intervals (1, 6, 12, 18, 24, 30 and 36 h). The equilibration time was found to be 24.0 h and was used in adsorption studies. 10 g soil samples and different % of biochar along with 0.01 M CaCl₂ solution of different concentration of NH₄NO₃, KH₂PO₄ and heavy metal (20 mL) solution were mixed in 80 mL glass stoppered test tubes. A control was maintained without biochar. To keep the ionic strength of the soil solution constant and to facilitate flocculation the CaCl₂ (0.01 M) was used as the background electrolyte. The mixture of soil, biochar and solution of ions was shaken for 20 min and equilibrated for 24 h followed by centrifuged the soil-water-biochar suspension at 300 rpm (10 min) in a centrifuge machine. Then it was filtered by filtration for analysis of N, P, K and heavy metal concentration. Difference between the concentrations of N, P, K and heavy metal in the original solution used for equilibration and those in the equilibrated solutions following reaction with the soil and/or biochar was used as the amount adsorbed.

NH₄⁺-nitrogen and NO₃⁻-nitrogen analysis

Ammonium N (NH⁺₄-N) was measured as pr the methodology of Keeney and Nelson (1982). Atfirst 10 g soil sample was taken in a beaker and extracted with 100 ml 2 M KCl solution. After extraction activated MgO was added into it and the content was steam distilled using micro-Kjeldahl distillation unit. During distillation process NH₃ was liberated and it was absorbed in 20 ml of 2% boric acid containing mixed indicator. Then it was continued to distillation until 100 ml of distillate was collected within a time of 3 min. Finally the distillate was titrated against 0.01 N H₂SO₄ till blue green colour disappear and solution tends to turn pink. 20 g soil sample was taken and 50 ml of distilled water added to it. Then it was shaken for 30 min followed by addition of a pinch of CaSO₄ or CaO, shaken for 10 min and allowed to stand for soil particle settling. It was then filtrated and concentrated using distillation flask after adding 1 gm MgO. The solution was cooled and 25 ml 0.02 N H_2SO_4 (or 5 ml boric acid indicator solution) was placed below the condenser. Then 1 gm of Devarda's alloy and 25 ml of 1% sodium hydroxide were added to the flak and it is connected to distillation apparatus. Till the evolution of NH₃ ceases completely, steam distillation was continued. In 10 ml of 4% boric acid indicator, the NH₃ gas evolved by steam distillation was absorbed. Then the absorbed NH₃ was titrated with 0.02 N H_2SO_4 till blue green colour disappear and solution tends to turn pink.

Available phosphorus and available potassium analysis

Available phosphorus was determined by Bray's-1 method. Atfirst Bray and Kurtz No. 1 extracting solution was prepared by dissolve 1.11 gm $NH_{4}F$ and 2.08 ml concentrated HCl and make upto 1 L. Then reagent 'A' was prepared by dissolving 6 g ammonium molybdate [(NH₄)₆MO₇O₂₄.4H₂O] in 125 ml distilled water and 0.1454 g antimony potassium tartrate [K(SbOC₄H₄O₆.¹/₂H₂O] in 50 ml distilled water. Then added these two solutions to 500 ml of 2.5 M H₂SO₄ and mixed thoroughly and make it to 2 L. Then reagent 'B' was prepared by dissolving 1.056 g ascorbic acid $(C_6H_8O_6)$ in 200 ml reagent 'A' and mixed. Then standard stock phosphorus solution (100 ppm) was prepared by dissolving exactly 0.439 g potassium dihydrogen orthophosphate (KH₂PO₄) in 500 ml distilled water. Then added 25 ml of 7 N H_2SO_4 into it and made to 1 L with distilled water. 2.5 gm of soil was taken and little activated charcoal was added. Then 25 ml extracting solution (Bray and Kurtz No. 1) was added into it and shaked for 5 min followed by immediate filter through Whatman no. 42. Then an aliquot of the extract was placed in a 25 ml volumetric flask. Then little distilled water was added and 4 ml of reagent B was also added, made up the volume with distilled water and mixed properly. After 10 min the intensity of blue colour was measured using a spectrophotometer at 730 nm along with the standards. Bray's phosphorus (kg ha⁻¹) = $(R \times 25 \times 2.24)/(5 \times 2.5)$; where $R = \mu g P$ in the aliquot. Available potassium was measured as per the method of Hanway and Heidel. In 5 gm of soil 25 ml of 1.0 N neutral (pH 7.0) ammonium acetate was added and mixture was shaken for 5 min on a shaker followed by immediately filter through Whatman No. 1. Then available K in the soil extract was measured by flame photometer. Available potassium (kg ha^{-1}) = $(R \times Volume of extract \times 2.24)/soil weight. Where; R=K$ (ppm) in the extract (obtained from the standard curve).

Statistical analysis

All the data generated during the entire period of investigation was statistically analysed using the 'F' using the procedure of Gomez and Gomez. LSD values at P=0.05 were used to determine the significance of difference between the treatment means. This analysis was done using the statistical package 'STATISTICS'.

Results and discussion

Biochar morpho-mineralogical characterization

Characterization of different biomass derived maize biochar produced at 400, 500 and 600 ^OC pyrolysis temperature has been shown in Table 1. The cation exchange capacity of biochar augmented with rise in pyrolysis temperature. The CEC is correlated with cations like Ca, Mg and K. Such variation in CEC among the biochar might be due to presence of different quantity of cations in different feedstocks (Das et al. 2021). Besides, increase in CEC with increase in temperature was associated with the augmentation in mineral nutrients, pH and EC. With increase in pyrolysis temperature the surface negative charges decreased and it was reported that low surface negative charges of biochar have protective ability for plants when applied in soil. With increase in charring temperature majority of the -COOH and -OH functional groups of biochar is reduced and thereby causes a noteworthy damage of surface negative charge. The hydrogen-bond has ability to reduce the surface negative charge while the oxygen bearing functional group may raise it (Mukherjee et al. 2020). The resulted biochar with higher porosity and BET surface area might have some positive effect on structural modification of soil and nutrient retention which can offer improved environment for beneficial soil microbiological growth and development. At low temperature pyrolysis the polarity index tends to increase and vice-versa. At low temperature pyrolysis (400 °C) the polarity index tends to increase and vice-versa. This depicted that biochar produced under low temperature results in more surface polar functional group and it does not depend on feedstocks type.

Scanning Electron Microscope of four different biochar produced at 600 ^OC has been presented in Fig. 1. The MSB showed highest cross-linked pores and featheryplate like layer construction on the surface of biochar, mainly the carbonaceous skeleton from the biological capillary structure of the feedstocks. Such porous structure on the biochar surface might lead to its high surface area. In our investigation the biochar samples retain some small holes and cracks due to generation of volatile substances during the process of carbonization. Transmission Electron Microscope of four different biochar produced at 600 ^OC has been presented in Fig. 1. Some black dots with nano-range (≤100 nm) particle size of different biochar produced under different temperature on the graphene-like surfaces were seen and these black dots were of crystalline stripes. The presence of crystalline stripes on black dots proved that the nano-range like sheets was haphazardly arranged in a tubostratic state (Das et al. 2023b, c, d, e). Fourier Transform Infra-red spectroscopy of four different biochar produced at 600 ^OC has been presented in Fig. 1. The strong and broad peak at 3450–3500 cm⁻¹ was due to due to alcoholic and phenolic O-H stretching (Roy et al. 2014). This may be due to existence of lignocellulosic components in the biochar. The band at $1550-1620 \text{ cm}^{-1}$ was due to aromatic C=O and C=C stretching vibration. After lignocellulosic substances condensation and decomposition, the derived products were responsible for such strong and broad peak. The above-mentioned analysis data seems to recommend huge prospective for MSB to adsorb plentiful positively charged toxic heavy metals and mineral nutrients (Bimbraw 2019). The MSB biochar produced at 600 ^OC was best regarding morpho-minerological properties and hence, it was considered for adsorption and desorption studies of soil mineral nutrients as well as heavy metals.

Adsorption of mineral nutrients in soil

Effect of manures and biochar additions on NH₄⁺-N and NO_3^{-} -N adsorption capacity has been presented in Fig. 2. In manure+biochar at 2.5+7.5 t/ha application rate the NH4⁺-N adsorption capacity was minimum in T₇ (15.9 and 117.66) followed by T_4 (17.6 and 130.24), T_{13} (18.7 and 138.38) and maximum in T_{10} (20.1 and 148.74) at 25 and 200 mg kg⁻¹ level of added NH₄⁺-N, respectively than control T_1 (10.3 and 75.3). Thus, increase in biochar application rate increased the NH₄⁺-N adsorption capacity. Beside manures also influenced the NH₄⁺-N adsorption. But the effect on adsorption was more with biochar than manures. In manure+biochar at 2.5+7.5 t/ ha application rate the NO3⁻-N adsorption capacity was minimum in T_4 (14.3 and 105.82) followed by T_{13} (16.4 and 121.36), T_7 (17.8 and 131.72) and maximum in T_{10} (19.2 and 142.08) at 25 and 200 mg kg⁻¹ level of added NO_3^{-} -N, respectively than control T₁ (7.34 and 54.23). Thus, increase in biochar application rate increased the

Table 1 Properties of different biochar produced at heterogeneous charring temperature and feedstocks sources

Feedstock	Temp (°C)	CEC (cmol P ⁺ kg ⁻¹)	Volatile mat- ter (%)	Porosity (%)	Polarity index	BET surface area (m² g ⁻¹)	C:N ratio	pH_{w}	рН _s	Fuel ratio
MSB	400	38.56	26.56	60.20	0.42	12.9	79	8.58	7.19	1.72
	500	47.60	20.67	62.70	0.28	23.2	85	9.38	8.07	2.33
	600	55.46	17.81	65.90	0.15	43.9	87	10.51	8.57	2.78



Fig. 1 SEM, TEM, EDS and FT-IR of maize biochar produced at 400, 500 and 600 $^{\circ}\mathrm{C}$

 $\rm NO_3^{-}-N$ adsorption capacity and positive effect was observed. An estimation of soil inorganic N availability in closed-loop organic farming systems has been suggested using soil $\rm NH_4^+-N$ levels. Biochar's comparatively greater CEC than soil, which results in a larger adsorption of free NH4+on biochar particles. Particularly in tropical regions with little soil fertility, nutrient leaking is frequently an issue.

The increase in the NH_4 -N adsorption site in the absence of biosolid was the cause of the rise in NH_4 -N adsorption with the addition of biochar. The primary cause of NH4-N adsorption in the soil/BC mixture is electrostatic force acting on negatively charged surfaces;

BC provides a source of negatively charged surfaces since it contains acidic organic groups. Nitrate leaching from the soil for longer than 25 and 67 days was said to be reduced by biochar made from pecan shells. Additionally, biochar has been reported to enhance nutrient retention, particularly N in tropical soils that get heavy rainfall. Effect of manures and biochar additions on PO₄^{3–}-P and K adsorption capacity has been presented in Fig. 3. In manure+biochar at 2.5+7.5 t/ha application rate the P adsorption capacity was minimum in T₄ (4.2 and 31.08) followed by T₁₀ (4.3 and 31.82), T₁₃ (4.4 and 32.56) and maximum in T₇ (4.5 and 33.3) at 25 and 200 mg kg⁻¹ level of added P, respectively than control T₁ (3.5 and 25.9).



Fig. 2 Effect of manures and biochar additions on NH₄⁺-N and NO₃⁻-N adsorption capacity

- NH4+-N adsorption at different levels of added NH4+-N (mg kg-1) 25
- NH4+-N adsorption at different levels of added NH4+-N (mg kg-1) 50
- NH4+-N adsorption at different levels of added NH4+-N (mg kg-1) 100
- NH4+-N adsorption at different levels of added NH4+-N (mg kg-1) 200
- NO3--N adsorption at different levels of added NO3--N (mg kg-1) 25
- NO3--N adsorption at different levels of added NO3--N (mg kg-1) 50
- NO3--N adsorption at different levels of added NO3--N (mg kg-1) 100
- NO3--N adsorption at different levels of added NO3--N (mg kg-1) 200



Fig. 3 Effect of manures and biochar additions on PO_{4}^{3} -P and K adsorption capacity

Thus, increase in biochar application rate increased the P adsorption capacity. Beside manures also influenced the P adsorption. But the effect on P adsorption was more with biochar than manures (Singh et al. 2018). In agricultural systems, phosphorus can play a major role as a limiting nutrient due to its high solubility, tendency to bind to the mineral surfaces of the soil, or complexation into forms that are difficult for plants to absorb. The increase in P sorption may be explained by exchangeable aluminium, which has been shown to precipitate as new, highly active P-adsorbing surfaces in soils or to co-precipitate with iron and aluminium oxides when soil pH is elevated. Furthermore, studies indicate that exchangeable Ca significantly affects P sorption because of Ca precipitation or co-sorption with the extra P. In manure+biochar at 2.5+7.5 t/ha application rate the K adsorption capacity was minimum in T_7 (13.3 and 98.42) followed by T_4 (14.7 and 108.78), T_{13} (15.1 and 111.74) and maximum in T_{10} (15.9 and 117.66) at 25 and 200 mg kg^{-1} level of added K, respectively than control T_1 (20.2 and 149.48).

Thus, increase in biochar application rate decreased the K adsorption capacity and negative effect was observed. P adsorption in the current study occurred either by a cation bridge with negatively charged biochar surface, which is heterogeneous in nature, or through a mix of physical and chemical adsorption, according to the best fitting of P adsorption to the Freundlich model (Southavong et al. 2018). Phosphorus serves a beneficial effect in the adsorption of heavy metals, and the enhanced rate is presumably connected to the difference in the accessible surface area of biochar samples (Das et al. 2023b, c, d, e).

Adsorption of heavy metal in soil

Effect of manures and biochar additions on Cd and Pb adsorption capacity has been presented in Fig. 4. In manure+biochar at 2.5+7.5 t/ha application rate the Cd



Fig. 4 Effect of manures and biochar additions on Cd and Pb adsorption capacity

adsorption capacity was minimum in T_{10} (6.24 and 43.05) followed by T_4 (6.76 and 46.64), T_{13} (7.47 and 51.5) and maximum in T_7 (7.75 and 53.47) at 10 and 100 mg kg⁻¹ level of added Cd, respectively than control T_1 (2.57) and 17.73). Thus, increase in biochar application rate increased the Cd adsorption capacity. Beside manures also influenced the Cd adsorption. But the effect on Cd adsorption was more with biochar than manures. In manure+biochar at 2.5+7.5 t/ha application rate the Pb adsorption capacity was minimum in T_7 (4.46 and 30.77) followed by T_{10} (4.71 and 32.49), T_{13} (5.16 and 35.60) and maximum in T_4 (5.48 and 37.81) at 10 and 100 mg kg⁻¹ level of added Pb, respectively than control T_1 (1.86 and 12.83).

Thus, increase in biochar application rate increased the Pb adsorption capacity and positive effect was observed. It's possible that raising the pH of the biochar-treated soils led to more sorption of Cd and Pb, which reduced their potential availability. Due to the less specific sorption of Cd, Cd was more exchangeable, but precipitation of anglesite minerals and lead phosphates enhanced Pb retention. The sorption of metals in the modified soils is evidently influenced by the ratios of compost to biochar, as indicated by the fitted sorption parameters and sorption isotherm curves. As more biochar was applied, the amounts of reducible, oxidizable, and residual forms of copper were found in the soil at higher rates. By regulating pH-dependent surface charges, enhancing exchange sites in soil amended with biochar, and limiting precipitation of Cd, soil pH played a critical role in enhancing Cd speciation. The liming impact of their alkaline chemical contents is what caused the biochar to create an elevation in soil pH and microbial activity. The process of pyrolysis transforms the metals present in the feedstock for biochar into (alkaline) oxides, hydroxides, and carbonates,

which are then integrated into the structure of BC particles.

The alkaline chemicals are dissolved by soil pore water, which raises the pH of the soil. Effect of manures and biochar additions on Zn and As adsorption capacity has been presented in Fig. 5. In manure+biochar at 2.5+7.5t/ha application rate the Zn adsorption capacity was minimum in T_7 (6.83 and 47.12) followed by T_{13} (7.21 and 49.74), T $_{\rm 10}$ (7.41 and 51.12) and maximum in T $_{\rm 4}$ (7.44 and 51.33) at 10 and 100 mg kg⁻¹ level of added Zn, respectively than control T_1 (6.28 and 43.33). Thus, increase in biochar application rate increased the Zn adsorption capacity. Beside manures also influenced the Zn adsorption. But the effect on Zn adsorption was more with biochar than manures. In manure+biochar at 2.5+7.5 t/ha application rate the As adsorption capacity was minimum in T_{10} (5.75 and 39.67) followed by T_4 (5.86 and 40.43), T_{13} (6.06 and 41.81) and maximum in T_7 (6.31 and 43.53) at 10 and 100 mg kg⁻¹ level of added As, respectively than control T_1 (4.41 and 30.42).

Thus, increase in biochar application rate increased the As adsorption capacity and positive effect was observed. Coordination with the amine group is known to have a major impact on the adsorption of transition metals, and this process frequently involves a homogeneous, singlelayer Langmuir process. The Langmuir model, however, did not work well with the isotherm data, and a number of earlier research revealed that lead adsorption on nonmodified biochar is a heterogeneous process. A change in soil pH may result in a reduction in the concentration of metals in the mobile forms of zinc and arsenic because free metal ions exhibit increased activity in low pH conditions (Al-Wabel et al. 2017). Metal solubility may also be decreased by the formation of metal complexes with organic waste. Because of the feedstock composition and



Fig. 5 Effect of manures and biochar additions on Zn and As adsorption capacity



Fig. 6 Effect of manures and biochar additions on N, P and K desorption

pyrolysis conditions, biochar generated at higher temperatures proves to be more effective than that produced at lower temperatures (Mukome & Parikh 2016). Numerous investigations have confirmed the efficacy of maize stalk biochar produced at high temperatures (Narzari et al. 2017). A different study stated that research revealed that the biochar made from peat moss had the highest maximal adsorption capacity for lead (Pb), followed by Cd and Cu.

Desorption of nutrients in soil

The reversible process of desorption in soil is closely linked to the bioavailability and adsorption reuse of the soil. One can determine the extent of desorption from the adsorptive materials by measuring the desorbability of the soil. Effect of manures and biochar additions on N, P and K desorption has been presented in Fig. 6. Results revealed that with increase in biochar application rate desorption of NH4+-N decreased. Desorption was more enhanced by poultry manure followed by FYM, vermicompost and goat manure. Similar trend was also observed for NO₃⁻-N and PO₄³⁻P where increase in biochar application rate decreased desorption. But interestingly increase in biochar application rate increased potassium (K) desorption.

Plant absorption and utilization of P are impacted by the limitation of soil P supply caused by P adsorption and desorption (Das et al. 2022). This happened because biochar has the ability to function as a soil conditioner, changing the microbiological and chemical characteristics of the soil and increasing the uptake of nutrients that would not have been available in otherwise unfavorable

- Zn adsorption at different level of added Zn (µg) 10
- As adsorption at different level of added As (ug) 25
- As adsorption at different level of added As (µg) 50
- As adsorption at different level of added As (ug) 100
- As adsorption at different level of added As (µg) 10
- As adsorption at different level of added As (µg) 25
- As adsorption at different level of added As (µg) 50
- As adsorption at different level of added As (µg) 100



- Cd desorption at different level of added Cd (%) 10
- Pb desorption at different level of added Pb (%) 100
- Zn desorption at different level of added Zn (%) 10
- As desorption at different level of added As (%) 100
- As desorption at different level of added As (%) 10
- As desorption at different level of added As (%) 100
- As desorption at different level of added As (%) 10
- As desorption at different level of added As (%) 100

Fig. 7 Effect of manures and biochar additions on Cd, Pb, Zn and As desorption

soils. When plant uptake of N is insufficient or when microbial activity is triggered by the need for biochar, some nutrients in the soil may mineralize into inorganic N (Yuan et al. 2015). When plant uptake of N is insufficient or when microbial activity is triggered by the need for biochar, some nutrients in the soil may mineralize into inorganic N.

Biochar contains energy substances that can act as microbial substrates, so using it as a soil N conditioner has the potential to increase fertilizer N retention in soil (Zhao et al. 2018). However, in some cases, N availability may decrease. These studies explain that the primary source of biochar's benefit was either the direct adsorption effect or the indirect microbial immobilization effect (İlay 2020).

Desorption of nutrients in soil

Effect of manures and biochar additions on Cd, Pb, Zn and As desorption has presented in Fig. 7. All the heavy metal Cd, Pb, Zn and As desorption decreased with increase in biochar application rate. Manures also significantly influenced desorption of Cd, Pb, Zn and As. Pb sorption on biochars may be facilitated by the binding mechanism, which is thought to be related to p-electrons and organic functional groups, particularly in soils that contain comparatively high levels of Pb.

The desorption rate of Cd first decreased and then rose as the biochar content increased in tandem with the pH change brought about by the interaction between compost and biochar. Changes in soil pH have a significant impact on the soil's affinity for metals, and are thought to be the primary factor influencing the adsorption and desorption of heavy metals in soil. Additionally, recent research demonstrated that adding charcoal to soil improved other soil parameters and clearly increased the pH and cation exchange capacity (CEC). Soil's total sorption capacity may have been enhanced by the use of biochar in our study, which would have decreased the mobility of heavy metals in the soil and, eventually, the levels of cadmium, lead, zinc, and arsenic. Additionally, according to a number of research, applying biochar reduced the amount of Cd in maize shoots (Das et al. 2020b).

This is likely because stable metal-organic complexes were formed (Xiao & Chen 2017). According to reports, increased soil aggregation leading to a higher waterholding capacity was correlated with enhanced nitrogen retention in the biochar-treated soil. Because they alter the pH and P sorption capacity of the soil, charcoal materials may also have an impact on the availability of P in the soil (Yadav et al. 2019). It's likely that adding char materials will lessen the amount of P that precipitates with Al and Fe when pH is raised in acidic soils, but that P availability will decrease in neutral or alkaline soils since the additional metals will improve P fixation.

Conclusions

The pyrolysis of biomass yields biochar, which can be utilised to combat nitrogen (N) pollution. We may now evaluate the most effective combination of compost and biochar in soil as the results showed that the different ratios of biochar and compost have a substantial impact on the sorption-desorption of metals in soil. This study indicates that the use of biochars as an inexpensive, efficient, and environmentally benign adsorbent to remove heavy metal pollution from the environment is a possibility. With increase in concentration the adsorption and desorption increased. Therefore, for the adsorption desorption of soil to increase food security, the selection of feedstock material for biochar formation and their application rates were crucial. The CEC of the biochars had the biggest impact on the adsorption of NH4+-N. At a pyrolysis temperature of 400 °C, the corn-straw biochar exhibited the highest adsorption capability for NH4+-N. We therefore conclude that biochars, especially cornstraw biochar (400 °C), can be employed in situations where NH4+-N (or NH3) pollution is an issue, but more investigation is required to determine the best way to use biochars to lower NO3-N pollution. From an economic point of view and mainly on the base of our results, we recommend the application of lower doses of biochar with higher dose of organic manure.

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Author contributions

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Data availability

No datasets were generated or analysed during the current study.

Declarations

Ethics approval and consent to participate Not applicable.

Competing interests

The authors declare no competing interests.

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References

- Al-Wabel MI, Hussain Q, Usman ARA, Ahmad M, Abduljabbar A, Sallam AS, Ok YS (2017) Impact of biochar properties on soil conditions and agricultural sustainability: a review. Land Degrad Dev 29(7):2124–2161
- Bimbraw AS (2019) Generation and Impact of Crop Residue and its management. Curr Agric Res Jurnal 7(3):303–309. https://doi.org/10.12944/CARJ.7.3.05
- Das SK, Ghosh GK (2021b) Development and evaluation of biochar based secondary and micronutrient enriched slow release nano-fertilizer for reduced nutrient losses. Biomass Convers Biorefinery. https://doi.org/10.1007/ s13399-021-01880-5
- Das SK, Ghosh GK (2021c) Hydrogel-biochar composite for agricultural applications and controlled release fertilizer: a step towards pollution free environment. Energy 242:122977. https://doi.org/10.1016/j.energy.2021.122977
- Das SK, Ghosh GK, Avasthe RK, Sinha K (2020b) Morpho-mineralogical exploration of crop, weed and tree derived biochar. J Hazard Mater 407:124370. https:// doi.org/10.1016/j.jhazmat.2020.124370
- Das SK, Ghosh GK, Avasthe R (2022) Biochar and organic manures on produce quality, energy budgeting, and soil health in maize-black gram system. Arab J Geosci 15:1527. https://doi.org/10.1007/s12517-022-10790-3
- Das SK, Ghosh GK, Avasthe RK (2023b) Conversion of crop, weed and tree biomass into biochar for heavy metal removal and wastewater treatment. Biomass Convers Biorefinery 3:4901–4914. https://doi.org/10.1007/ s13399-021-01334-y
- Das SK, Ghosh GK, Avasthe RK, Choudhury BU, Mishra VK, Kundu MC, Roy A, Mondal T, Lama A, Dhakre DS (2023c) Organic nutrient sources and biochar technology on microbial biomass carbon and soil enzyme activity in

maize-black gram cropping system. Biomass Convers Biorefinery 13:9277–9287. https://doi.org/10.1007/s13399-021-01625-4

- Das SK, Ghosh GK, Avasthe RK, Kundu MC, Choudhury BU, Baruah K, Lama A (2023d) Innovative biochar and organic manure co-composting technology for yield maximization in maize-black gram cropping system. Biomass Convers Biorefinery 13:7797–7809. https://doi.org/10.1007/s13399-021-01519-5
- Das SK, Ghosh GK, Mishra VK, Choudhury BU, Dutta SK, Hazarika S, Kalita H, Roy A, Singh NU, Gopi R, Devi EL, Mukherjee I, Balusamy A, Singh M, Yadav A, Kapoor C, Baruah K (2023e) Utilizing dissimilar feedstocks derived biochar amendments to alter soil biological indicators in acidic soil of Northeast India. Biomass Convers Biorefinery 13:10203–10214. https://doi.org/10.1007/ s13399-021-01670-z
- İlay R (2020) Short-lived effects of Olive Pomace Biochar produced at different temperatures on nitrate (NO3 -), Bromide (Br-), sulfate (SO4 2-) and phosphate (PO4 3-) leaching from Sandy Loam Soils. Commun Soil Sci Plant Anal 1–21. https://doi.org/10.1080/00103624.2020.1822375
- Kang Z, Jia X, Zhang Y, Kang X, Ge M, Liu D, Wang C, He Z (2022) A review on application of Biochar in the removal of Pharmaceutical pollutants through Adsorption and Persulfate-based AOPs. Sustainability 14(16):10128. https:// doi.org/10.3390/su141610128
- Kavitha B, Reddy PVL, Kim B, Lee SS, Pandey SK, Kim KH (2018) Benefits and limitations of biochar amendment in agricultural soils: a review. J Environ Manage 227:146–154
- Keeney DR, Nelson DW (1982) Nitrogen-inorganic forms. In: Page AL (ed) Methods of soil analysis, agronomy monograph 9, part 2, 2nd edn. ASA, SSSA, Madison, WI, pp 643–698
- Liu G, Zhang X, Liu H, He Z, Show PL, Vasseghian Y, Wang C (2023) Biochar/layered double hydroxides composites as catalysts for treatment of organic wastewater by advanced oxidation processes: a review. Environ Res 234:116534. https://doi.org/10.1016/j.envres.2023.116534
- Luo D, Wang L, Nan H et al (2023) Phosphorus adsorption by functionalized biochar: a review. Environ Chem Lett 21:497–524. https://doi.org/10.1007/s10311-022-01519-5
- Mukherjee I, Das SK, Kumar A, Shukla L (2020) Sludge amendment affects the persistence, carbon mineralization and enzyme activity of atrazine and bifenthrin. Bull Environ Contam Toxicol 105(2):291–298
- Mukome FND, Parikh SJ (2016) Chemical, physical, and surface characterization of biochar. In: Ok YK, Uchimiya SM, Chang SX, Bolan N (eds) Biochar: production, characterization, and applications. CRC Press, Boca Raton, FL, USA, pp 67–96
- Narzari R, Bordoloi N, Sarma B, Gogoi L, Gogoi N, Borkotoki B, Kataki R (2017) Fabrication of biochars obtained from valorization of biowaste and evaluation of its physicochemical properties. Bioresour Technol 242:324e328. https://doi. org/10.1016/j.biortech.2017.04.050
- Roy A, Dkhar DS, Tripathi AK, Singh NU, Kumar D, Das SK, Debnath A (2014) Growth performance of agriculture and allied sectors in the north east India. Economic Affairs 59(Special):783–795
- Singh M, Gupta B, Das SK (2015) Assessment of Economic viability of different Agroforestry systems in Giri Catchment, Himachal Pradesh. Economic Affairs 60(3):557–561
- Singh M, Gupta B, Das SK (2018) Soil organic carbon density under different agroforestry systems along an elevation gradient in north-western Himalaya. Range Manage Agrofor 39(1):8–13
- Sixu Ren S, Wang Y, Liu Y, Wang, Feng Gao &Yingjie Dai (2023). A review on current pollution and removal methods of tetracycline in soil 2578–2602. https://doi.org/10.1080/01496395.2023.2259079
- Southavong S, Razi IM, Preston TR, Halimi MS, Roslan I (2018) Effects of Pyrolysis temperature and Residence Time on Rice Straw-derived Biochar for Soil Application. Int J Plant Soil Sci 23:1e11. https://doi.org/10.9734/ IJPSS/2018/42197
- Tan Z, Zou J, Zhang L, Huang Q (2018) Morphology, pore size distribution, and nutrient characteristics in biochars under different pyrolysis temperatures and atmospheres. J Mater Cycles Waste Manag 20:1036e1049. https://doi. org/10.1007/s10163-017-0666-5
- Wang M, Zhu Y, Cheng L, Andserson B, Zhao X, Wang D, Ding A (2018) Review on utilization of biochar for metal-contaminated soil and sediment remediation. J Environ Sci 63(1):156–173
- Wang C, Luo D, Zhang X, Huang R, Cao Y, Liu G, Zhang Y, Wang H (2022) Biocharbased slow-release of fertilizers for sustainable agriculture: a mini review. Environ Sci Ecotechnology 10:100167
- Waqas M, Aburiazaiza AS, Miandad R, Rehan M, Barakat MA, Nizami AS (2018) Development of biochar as fuel and catalyst in energy recovery technologies. J Clean Prod 188:477–488

- Xiao X, Chen B (2017) A Direct Observation of the fine aromatic clusters and molecular structures of Biochars. Environ Sci Technol 51(10):5473–5482. https://doi.org/10.1021/acs.est.6b06300
- Yadav K, Tyagi M, Kumari S, Jagadevan S (2019) Influence of process parameters on optimization of biochar fuel characteristics derived from rice husk: a promising alternative solid fuel. Bioenergy Res 12:1052–1065. https://doi. org/10.1007/s12155-019-10027-4
- Yingjie Dai Y, Liu Y, Wang W, Fang Y, Chen YS (2023) A Practice of Conservation Tillage in the Mollisol Region in Heilongjiang Province of China: A Mini Review. Pol. J. Environ. Stud. 2023;32(2):1479–1489 https://doi.org/10.15244/ pjoes/156473
- Yuan H, Lu T, Huang H, Zhao D, Kobayashi N, Chen Y (2015) Influence of pyrolysis temperature on physical and chemical properties of biochar made from sewage sludge. J Anal Appl Pyrol 112:284e289
- Zhang A, Cheng G, Hussain Q, Zhang M, Feng H, Dyck M, Wang X (2017) Contrasting effects of straw and straw–derived biochar application on net global warming potential in the Loess Plateau of China. Field Crops Research 205:45–54
- Zhao N, Lv Y, Yang X, Huang F, Yang J (2018) Characterization and 2D structural model of corn straw and poplar leaf biochars. Environ Sci Pollut Res 25:25789–25798

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