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Evaluating the environmental and agronomic implications of bone char and biochar applications to loamy sand based on sorption data

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Abstract

Background The widely adopted use of charred biomass for agronomic and environmental purposes; and the reported positive and deleterious effects necessitated the need for this study to ascertain the potential causes of the erratic results surrounding the use of charred biomass in agriculture and the environment. A batch sorption experiment was carried out to determine the sorptive and desorptive capacity of bone char and biochar on nitrate, ammonium, phosphate and sulphate concentrations in a loamy sand soil. The potential agronomic and environmental implications of the sorption data were also discussed.

Results The results indicated that bone char is richer in nutrient composition than biochar, with 70% more ability to sorb nutrients. The bone char and biochar sorption isotherms conformed to the H-curve isotherm type. Bone char and biochar have multiple layers of adsorption sites. Nutrient adsorption maxima, binding energy, and maximum buffering capacities of the soil were increased with the addition of bone char and biochar. The unamended soil was observed to retain as low as 6% of added nitrate to as much as 58% of added phosphate, while bone char retained 56% of added sulphate, 47% of phosphate, 76% nitrate and 64% of ammonium. Generally, bone char retained 60.6% of the added nutrients, while biochar retained 40.7% of the nutrients. The addition of bone char led to a 45.8% increase in the nutrient retention ability of the soil and a 36.1% increase with the addition of biochar.

Conclusion The nutrient sorption characteristics of biochar should be studied prior to its use as a soil nutrient amendment. It was concluded that bone char or biochar is a potential soil nutrient immobilizer; hence, applications for agronomic purposes should take cognizance of the native soil fertility so as to appropriately add fertilizer input before use.

Keywords Bone char, Biochar, Soil nutrients, Sorption isotherms, Adsorption, Desorption, Immobilization

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Background

The recycling of organic wastes in the raw or processed forms is a world-wide popular practice. This is partly because of the need to reduce and reuse waste materials and to eventually ensure environmental sustainability. The use of processed organic wastes in agriculture has been advocated by scientist and is popularly being adopted, particularly by organic agriculture practitioners basically because of its relative affordability and also due to its environmental friendliness (Piccirillo 2023).

Animal bones, wood shavings, and sawdust are major waste generated from animal-meat and forestry enterprises, particularly in tropical Africa where animal meats are processed almost manually and where timbers are sawed and smoothed using crude equipment. One of the alternative ways of using animal bones is the incineration of the bones and the resulting ash used as bone meal in the poultry industry. This is the common practice in sub-Saharan Africa, but the current use of the bone as a feed material in the production of bone char is gaining popularity (Amalina et al. 2022). Wood shavings and saw dust are relatively more abundant and constitute environmental nuisance in saw mills in south western Nigeria and other sub-Saharan African countries. This menace has necessitated the need to look for alternative use of the waste. This has resulted into the conversion of the saw dust and wood shavings into ashes and their subsequent application as liming materials, this, however is known to contribute to the carbon-dioxide pool in the atmosphere and hence, contributing to global warming.

The agronomic use of biochar made from wood shavings has wide acceptance in Africa but little is known of bone char. The agronomic importance of the application of charred organic materials from either plant or animal origins is enormous. Several works have reported the improvement in the soil's ability to supply nutrients and the overall improvement in soil physical, microbiological, and chemical properties (El-naggar et al. 2019; Irfan 2017; Tomczyk et al. 2020; Gu 2021). Application of biochar has also been reported to increase the yield of crops grown in the soils to which the biochar has been applied (Li et al. 2018; Azeem et al. 2021). The use of biochar in environmental studies in the developed countries are well documented in literatures (Hassan and Carr 2021; Talaiekhozani et al. 2021) but not much of such studies have been done or reported in the sub-Saharan African countries, this is majorly due to the wide popularity and the use of biochar amongst agronomists but less by the local environmentalists. Biochars properties have been documented to be dependent on the types of feedstock and the pyrolysis temperature (Rashid et al. 2019). The structural and elemental assessment of biochars has earlier been reported to assists in anticipating their specific ecological impact (Li et al. 2016).

Usually the fibrous structures of the wood shavings or sawdust and the hard texture of bone were retained after the pyrolysis except that the carbon skeleton of the feedstock are gotten as the biochars or bone char, respectively. Characteristically, biochar/bone char is reported to contain some functional groups like C–O, C=O, and −OH, and these groups have been indicated to be in organic functional groups (Inyang et al. 2011; Uchimiya et al. 2011), and responsible for the sorption of metals, nutrients and removal of contaminants like heavy metals and other functionally active metallic contaminants (Yaashikaa et al. 2020). Additionally bone char has been reported to contain calcium phosphate and often hydroxyapatite; with high surface area around 101.79 $m^2\ g^{-1}$ for bone char at 700 °C, with mesopores of about 6 nm (Samsami et al. 2020., Chagtmi et al. 2022). However, the type and magnitude of the functional groups of biochar have been reported to be temperature dependent (Yaashikaa et al. 2020) among other factors. The combination of calcium phosphate and graphitic carbon makes bone char a unique material different from ordinary biochar from plant sources and with different possible uses (Piccirillo 2023). However, studies on the comparative effectiveness of the different types of biochars from plant and animal sources are lacking or few in literatures.

In sub-Saharan Africa, the use of biochar in improving soil fertility is extensive and widely reported in literatures, this is hinged on the assumption that the biochar will temporarily hold plant nutrients, prevent them from being leached and later release the nutrients for plant uptake. This agronomic intervention is based on the ability of biochar to sorb and desorb held nutrients. The stability of biochar is a key factor to be considered prior to its application for either agronomic or environmental purposes (Han et al. 2020; Leng et al. 2019). The strength of the carbon structure formed by biochar is dependent on the nature and geometrical presentation of the constituents of carbon bonds (Tang et al. 2019).

Agricultural land faces a great deal of challenges due to the loss of mineral nutrients in the soil. Nevertheless, incorrect fertilizer application has raised input costs and may have detrimental effects on the environment in an attempt to improve soil fertility and nutrient management (Sun et al. 2019) such as eutrophication through nutrient leaching and runoff (Xu et al. 2019). It is essential to control losses and enhance retention of nutrients using inexpensive, reliable, dependable and environmentally friendly materials.

Despite this growing popularity on the use of biochar, little or no studies have been reported on the comparative effects of different feed stocks on the quality of the charred products, their effect on nutrient sorption and the potential implications on the environment. The foregoing becomes germane because the potential impact of biochar usage on the environment needs to be investigated to minimize unwanted consequences. Moreso, earlier workers (D'Hose et al. 2020) have reported that both positive and deleterious effects were observed with the application of biochars to fields, however, the effects need to be studied widely before any adoption of the use of these amendments (Ghodszad et al. 2021).

Thus establishing the agronomic and environmental implications of biochar in soil, consequently, this study was conducted to evaluate the ammonium, nitrate, phosphate and sulphate sorption characteristics of biochar (made from sawdust) and bone char (from animal bones) applied to soil.

Materials and methods

Soil sampling and analyses

The sorption study was carried out on a Ferric Luvisols. The soil was collected from a site within the Federal University of Agriculture, Abeokuta (FUNAAB) located in the derived Savannah agro-ecological zone of Nigeria (N7° 14' 21" E3° 26' 89"). Soil samples were collected from a nutrient exhausted farmland predominantly grown to maize (*Zea mays*) and cassava (*Manihot esculentus*). Collected composite sample was homogenized, air-dried, pulverized, sieved with 2 mm mesh size and some physical and chemical properties were determined by standard procedures as outlined below.

The prepared soil sample was analyzed for particle size distribution by the hydrometer method as described by Bouyoucos (1951) after the soil dispersion using sodium hexametaphosphate. Soil pH was determined in a 1:2 soil to water ratio using a glass electrode pH meter (McLean 1982). The total dissolved salt in the soil was measured as the soil electrical conductivity (EC) as described by Jackson (1963). This was measured in soil suspension by the method of Kalra and Maynard (1991). Total organic carbon (TOC) was determined using chromic acid oxidation procedure of Nelson and Sommer (1996). The exchangeable sodium (Na), potassium (K), calcium (Ca) and magnesium (Mg) in the soils were extracted with 1 N NH_4OAc buffered at pH 7. The extracted Ca and Mg were determined by Atomic Absorption Spectrophotometer (AAS) while extracted Na and K were determined by Flame Photometer. Total nitrogen (N) was determined by modified Micro-Kjeldahl digestion technique as described by Jackson (1963). Nitrate and ammonium - N were extracted with K_2SO_4 and determined colourimetrically (Cataldo et al. 1975) using a UV/Visible Spectrophotometer at a wavelength of 410 and 655 nm, respectively. Available phosphorus (P) concentration of the soil was extracted with by the Bray-1 procedure (Bray and Kurtz 1945) and determined using molybdate blue method (Murphy and Riley 1962) at 882 nm wavelength. Available sulphur (S) was extracted in in 0.01 M $CaCl_2$ determined by the turbidimetric procedure of Chesnin and Yien (1951) using a UV/Visible Spectrophotometer at a wavelength of 420 nm.

Biochar feed-stocks and Processing

The feed-stocks that were used for the production of biochar were cattle bones and wood shavings. The bone char (AB) was made from animal bones collected from an abattoir composed majorly of humerus, ulna, tibia, femurs and ribs, while the biochar (PB) was made from wood shavings/sawdust, collected from a commercial sawmill, and it is composed mainly of *Gmelina arborea* and *Swietenia mahagoni*. The collected feed-stocks were sun-dried before charring. Animal bones were oven dried at 120℃ for 24 h to further remove all the fat content. Feed-stock was charred at a temperature of 350℃, according to Eduah et al. (2019) using a pyrolysis reactor (locally fabricated and temperature-controlled pyrolizer). After pyrolysis, bone char and biochar were allowed to cool, pulverized and sieved through a 2 mm mesh size. Each feed-stock (bone char and biochar) was weighed before and after charring to determine the biochar yield. Biochar yield is the proportion of the weight of pyrolysis product to the weight of the feed-stock.

Sorption Experiment

Varying standard solutions of nitrate-N, ammonium-N, phosphate and sulphate-S which were prepared separately from 1000 mg kg^{-1} KNO_3, $(NH_4)_2SO_2$, KH_2PO_4, and K_2SO_4 solutions, respectively. Two (2) g of soil, 2 g of AB, 2 g of PB, 1 g of soil + 1 g of AB, and 1 g of soil + 1 g of PB were weighed into several plastic bottles and 30 ml of adsorbates (NO_3^-, NH_4^+, PO_4^{3-} and SO_4^{2-}) solutions of varying concentrations (0, 5.0, 10.0, 20.0, 25.0, 50.0, 75.0 and 100.0 mg L^{-1}) prepared from the standard solutions, in three replications. In addition to the adsorbates, a weak 0.01 M KCl was used as background electrolyte. These were shaken with the aid of mechanical shaker at 400 rpm for one (1) hour, the samples were allowed to stand for 24 h to achieve adsorption equilibrium before NO_3^-, NH_4^+, PO_4^{3-} and SO_4^{2-} adsorbed were quantified using the UV/V Spectrophotometer using the methods mentioned earlier. The amount of nutrient adsorbed by the soil / AB / PB and their mixtures were calculated from the differences between the amounts found in the filtrate and the initial amount in the solution using the following equation (Azeez et al. 2014).

$$Q = [(C_0 - C_e) \times V]/m \quad (1)$$

where C_0 and Ce (mg L^{-1}) are the liquid-phase concentrations of adsorbate initially and at equilibrium, respectively. V is the volume of the solution (ml), m is the mass of dry adsorbent (g), Q (mg kg^{-1}) is the amount of adsorbed at equilibrium.

The sorption efficiency (%) and amounts of adsorbate (Q) by soil, AB, PB or their mixtures with the soil was estimated as:

$$\text{Sorption efficiency }(\%) = [(C_0 - C_e)/C_0] \times 100 \quad (2)$$

where C_0 and Ce (mg L^{-1}) are the liquid-phase concentrations of adsorbate initially and at equilibrium, respectively.

The sorption data was evaluated for their conformity to both Freundlich and Langmuir isotherm models. The Langmuir isotherm is applied to monolayer adsorption on homogeneous sites, whereas the Freundlich isotherm suites are applied to multilayer adsorption on heterogeneous sites.

Freundlich adsorption equation is an empirical relation between the amount of substance adsorbed (K_f) per unit mass of the adsorbate (Q) and the aqueous concentration (C). The logarithmic form of the Freundlich isotherm model is as follows:

The Freundlich equation is given by:

$$\text{In } Q = \text{In } K_f + (1/n) \text{ In } C \quad (3)$$

Where: Q is the adsorbate adsorbed in mg kg^{-1}, C is the equilibrium concentration in mg L^{-1}, K_f (L mg^{-1}) and n (slope of the graph) are empirical constants. 1/n ranges between 0 and 1, and is a measure of adsorption intensity. A lower 1/n value indicates a greater degree of heterogeneity on the adsorbent surface. The parameter n is usually greater than unity. Typically, 1/n values range from 1 downwards. The parameter K_f indicates the Freundlich adsorption capacity, while the parameter n characterizes the heterogeneity of the system reflecting adsorption intensity (binding energy) (Gutema et al. 2023).

The linearized form of Langmuir equation can be written following (Alfaro-Cuevas-Villanueva et al. 2014; Salarirad and Behnamfard 2011) as:

The Langmuir equation is given by:

$$C/Q = 1/K_L b + C/b \quad (4)$$

Langmuir parameters were determined from the regression line of a plot C/Q against C values where 1/b is the slope, b (adsorption maximum; mg kg^{-1}) is the reciprocal of the slope of that plot. The intercept is 1/ K_Lb, and K_L (L mg^{-1}) is the binding energy evaluated as slope/intercept. The Langmuir constant (K_L) indicates the extent of interaction between adsorbate and the surface. If the value of K_L is relatively larger it indicates that there is a strong interaction between adsorbate and adsorbent while smaller value implies a weak interaction. K_Lb is Langmuir constant related to the sorption energy, it is the affinity of adsorbent toward the adsorbate. High value of K_L implies strong binding.

The maximum buffering capacity (MBC) was calculated by multiplying sorption coefficients b and $\mathbf{K_L}$ (Kuo 1990).

$$\text{MBC} = b \times K_L \quad (5)$$

Desorption Experiment

To investigate the release of adsorbed NO_3^-, NH_4^+, PO_4^{3-} and SO_4^{2-} from the adsorbent surfaces. After the adsorption study, the adsorbate solutions remaining in the bottles were decanted; 30 ml of a weak KCl solution of 0.01 M (Zhang et al. 2016) was added as a background electrolyte to the bottles and shaken with the aid of mechanical shaker at 400 rpm for one (1) hour and was allowed to stand for 24 h. The NO_3^-, NH_4^+, PO_4^{3-} and SO_4^{2-} concentration in the supernatant were determined. The number of desorbed adsorbates was estimated by subtracting the amount of NO_3^-, NH_4^+, PO_4^{3-} and SO_4^{2-} that was calculated to be in the amount the solution from the amount in the adsorbent.

$$\text{Percentage retained is estimated as} = \frac{\textit{sorbate adsorbed} - \textit{sorbate desorbed}}{\textit{sorbate adsorbed}} \times 100 \quad (6)$$

Data Analysis

Data generated were analyzed using Microsoft Excel. Means and standard deviations of the observations were estimated and the standard errors of the means were also used for comparisons.

Results and discussion

Properties of the soil, biochar and bone char used for the experiment and their implications

The bone char yield was 74.08% while that of biochar made from wood-shavings was 52.97%. The properties of the soil, bone char and biochar used for the experiment are shown in Table 1. It was evident that the soil was neutral in reaction while the exchangeable cations were all low in amounts. The soil total nitrogen was low but the organic carbon and phosphorus in the soil are moderate in amount. The micro-nutrient content of the soil was moderate in quantity. The textural analysis of the soil indicated that the soil had 834 g kg^{-1} sand, 68 g kg^{-1} silt and 98 g kg^{-1} clay. The soil is classified as loamy sand. The low chemical properties and some other soil fertility indices is an indication that there is the need for nutrient addition to the soil if the productivity is to be sustainable. It has earlier been reported that the soil collected from a field that has been cropped for more than five years

Table 1 Properties of soil and materials used for the experiment

Experimental material	pH	Exchangeable bases				Total	Total	Avail. / Total	Micro-nutrients			
		Ca	Mg	Na	K	N	Org C	P	Mn	Fe	Cu	Zn
		cmol kg^{-1}				%		mg kg^{-1}				
Soil	7.23	2.28	0.67	0.27	0.11	0.11	1.56	17.17	34.05	6.51	1.76	6.22
Bonechar/Biochar		Total (%)				%		mg kg^{-1}				
Animal Biochar	7.83	0.76	0.32	0.26	0.42	0.26	7.39	923.25	109.38	307.25	3.13	33.75
Plant Biochar	7.58	0.12	0.10	0.13	0.14	0.18	14.45	169.31	9.63	102.00	2.01	23.88

without fertilization and hence the low amounts of the soil fertility indicators is justified. The textural class of the soil also shows that the native or applied nutrients to the soil needs to be made resident in the soil and prevented from leaching before any gains from investments in soil amendments can be achieved. This is one of the reasons for the addition of biochar and other amendments like fertilizer and compost to the soils of this region.

The properties of the bone char and biochar presented on Table 1 reveals that both materials were basic in reaction with the bone char having the highest pH in water. Both the biochar and bone char were alkaline, which is common for thermally produced biochars (Lehmann and Joseph 2009), and canbe used as liming materials in acidic soils. The bone char used in this study was richer in nutrients than the biochar. It had higher Ca, Mg, Na, K and nitrogen compared with the biochar. These differences in nutrients are a reflection of the quality of the feedstock used in producing the biochar (Rashid et al. 2019). The sawdust /wood shavings are more fibrous and poorer in basic nutrients except carbon. The high carbon content of the biochar is typical of pryrolyzed material and consistent with the results of (Inyang et al. 2011; Zimmerman et al. 2011). Also the higher C in the biochar is consistent with the results of Tomczyk et al. (2020), who reported that biochars produced from animal litter and solid waste feedstocks exhibit lower carbon content, volatile matter and high CEC compared to biochars produced from crop residue and wood biomass, due to the lignin and cellulose content of the feedstock.

The total phosphorus and micro-nutrient content of the bone char is also higher than the biochar (Table 1). Generally, bone char has been reported be to richer in Ca, P and often hydroxyapatite (Pinheiro 2021), this has made it a slow release source of nutrients to soil. The versatility and richness in nutrients have made it a potential material for many purposes (Piccirillo 2023). The higher amount of graphite carbon makes bone char better adsorbent of metals and soil nutrients than the counterparts from plant sources.

Ammonium - N, nitrate - N, phosphate and sulphate sorption indices

The graphical presentation of the relationship between the amount of nutrients added and the amount sorbed by the soil and bone char / biochars are shown in Fig. 1. It is clearly evident that the sorbed amount of NO_3^-, NH_4^+, PO_4^{3-} and SO_4^{2-} by the soil is proportional to the amount added to the soil or bone char / biochar. The amount of sulphate sorbed by the soil was significantly lower than the amount sorbed by the bone char, biochar and the mixtures of the bone char / biochar with soil. The Figure clearly shows that the bone char had the highest capacity to sorb sulphate followed by

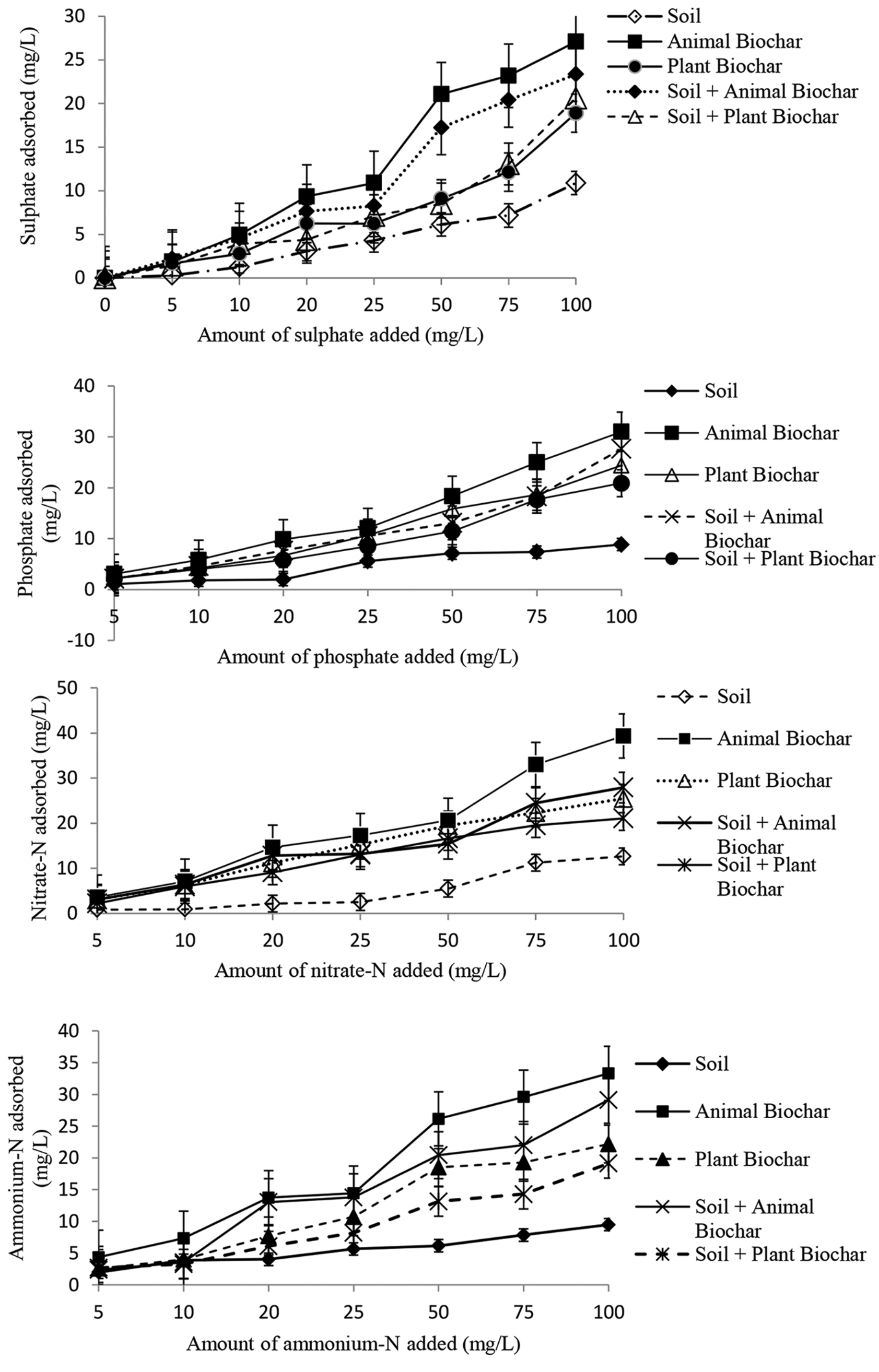

Fig. 1 Sorption of nutrient by soil, bone char, biochar and their combinations

biochar, then biochar+soil mixture and the least in the soil alone. A clear demarcation on the sorptive abilities of the material was shown at higher concentration of the nutrients added to the soil. The low ability of the soil to sorb SO_4^{2-} was however, enhanced significantly by the addition of either bone char or biochar amendments. The trend observed in the sorption of NO_3^-, NH_4^+ and PO_4^{3-} are similar. It was also observed that the soil had the lowest amounts of the nutrients sorbed, this was significantly lower than the amounts observed for other treatments. More than triple the amount of phosphate sorbed by the soil was recorded in bone char alone at the application of 100 mg PO_3^{4-} L^{-1}. Similar magnitude was observed in nitrate and ammonium sorption at this rate.

In general, the addition of bone char to the soil significantly improved the sorption of NO_3^-, NH_4^+ and PO_4^{3-} by the soil. Mizuta et al. (2004) had earlier reported that bamboo biochar had relatively higher nitrate adsorption capacity. The incremental value was higher than those observed by the addition of the biochar alone. On the average, across the four nutrients, the order of nutrient sorption ability is as follows: bone char > bone char + soil > biochar > biochar + soil > soil alone. This shows that bone char has more ability to sorb nutrients like NO_3^-, NH_4^+, PO_4^{3-} and SO_4^{2-} than its counterparts from the plant source, this has also improved its ability to positively enhance the sorptive abilities of the soil. Earlier works have indicated that bone char has larger surface area compared with biochar and thus more sites where the nutrients could be anchored against leaching. Similar results have been reported for bone char in the sorption of metals and other contaminants, perhaps because bone char have been reported to be more effective at removing cationic species from solution because of their relatively higher net negative surface charge (Beesley et al. 2011; Lehmann et al. 2011).

The superior ability of the bone char and biochar at sorbing nutrients particularly at higher concentration above the soil alone establishes the potential usefulness of the addition of the charred material to areas with accidental over-fertilization and also spillage of contaminants. The bone char / biochar have also proved that the large surface area and the likely charges can accommodate anions and cations on their exchange sites. This result also shows that the sole application of bone char or biochar will have potential detrimental effect for nutrients availability. Application of the materials without a complementary nutrient source could lead to temporary immobilization of the native soil nutrients. Such will deprive plants nutrients needed for growth and development.

While considering the effects of feedstock type on nitrate, sulphate, and phosphate sorption, bone char has a greater nutrient-sorption capacity. However, biochar surfaces are frequently negatively charged, which attracts positively charged ions like ammonium. The bone char's high cation-exchange capacity (CEC) values indicated the capacity to sorb more anions than cations. Given that Ca and Mg were present in bone char in relatively higher abundances; higher sorption of nitrate, sulfate, and phosphate is expected. This is because these nutrients may precipitate with Ca and Mg.

The sorption isotherms of the different materials for each nutrient were identical. Figure 2 shows the sorption isotherm of bone char and biochar for phosphate as a representative of the sorption behaviour for other materials and nutrients. The isotherms conformed to the H-curve isotherm type, which is an indication of the strong affinity between the adsorbent (soil) and the absorbate (ions), particularly at lower concentrations of the adsorbate. The Figure also shows the evidence of probable multiple sites of adsorption for the phosphate. This trend was observed

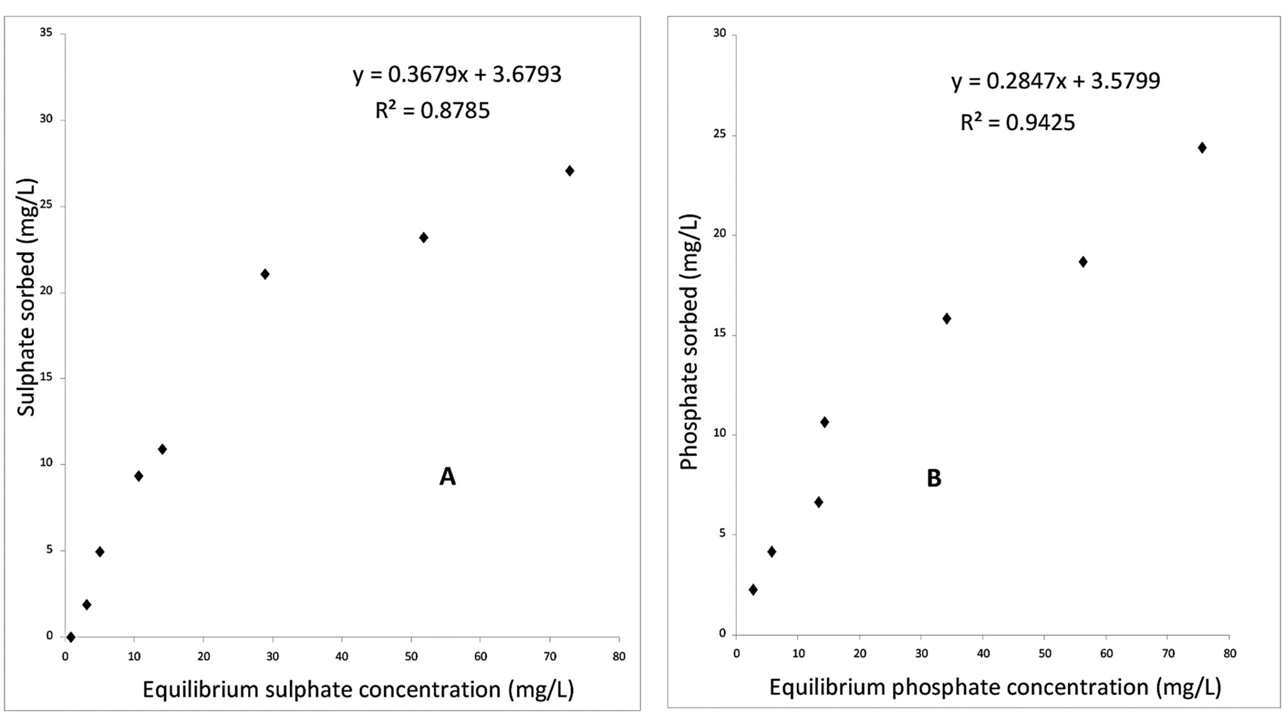

Fig. 2 Sulphate and phosphate sorption isotherms by bone char and biochar sample. A = Bone char; B = Biochar

Table 2 Slope of the isotherms (generalized data cross energy levels)

	Slope of isotherms			
	Sulphate	Phosphate	Nitrate	Ammonium
Soil	0.1145	0.0865	0.1571	0.0733
Animal Biochar	0.3679	0.3953	0.5355	0.4195
Plant Biochar	0.2013	0.2847	0.2689	0.2554
Soil + Animal Biochar	0.3056	0.3126	0.3112	0.3326
Soil + Plant Biochar	0.2228	0.2419	0.2176	0.2008
Sdev. ±	0.098	0.114	0.145	0.131
mean	0.242	0.264	0.298	0.256

for the soil, the bone char, biochar and their mixtures for all the nutrients studied. Phosphate is known to be specifically adsorbed because the amount of it sorbed is usually more than the amount that could solely be explained by electrostatic interactions alone. For such occurrence, phenomena such as ligand exchange and / or anion penetration have been opined as possible additional mechanisms for the elevated amount of phosphate sorption. The multiple layers observed in the bone char and biochar could perhaps be suitable for such multiple layers of nutrient sorption. The tenacity of adsorption as measured by the slope of the isotherm is higher at lower equilibrium concentration between 2 and 20 mg L^{-1} while the slope is lower at equilibrium concentration of > 20 mg L^{-1}.

This generally divides the adsorption energies into two. In Table 2, the slope of the isotherms as a measure of the tenacity or magnitude of nutrient sorbed is shown. The data indicated that bone char sorbed more nutrients than other materials considered in this study; this is closely followed by the soil + bone char mixture and least in the soil alone. The positive effect of adding bone char or biochar to improve the sorption ability of the soil is also shown. In other to adequately capture the behaviour of the bone/biochar, soil and their mixture at the two energies of adsorption, the sorption data were divided into two and the sorption characteristics at each level was computed. The slope of the sorption isotherm is shown in Table 3. It is observed that the nutrients were held more tenaciously at lower equilibrium concentrations by the bone char followed by its mixture with soil and to a lower extent by the biochar, similar trend was observed at equilibrium concentrations at > 20 mg L^{-1}. This shows that ability of the bone char or biochar to sorbed the nutrients are higher at lower equilibrium concentrations. This suggests that because the biochar material had more sorption sites and caused NO_3^-, PO_4^{3-}, and SO_4^{2-} to precipitate with the basic ions, the biochar materials showed higher binding energies of the ions sorbed at lower concentrations than at higher concentrations.

This shows that their sites of adsorption are finite and should be considered before being deployed as amendments for nutrient management or for environmental cleaning purposes. This also implies that the application of biochar for agronomic purposes needs to take cognizance of the native nutrient status of the soil so as to appropriately add the exogenous fertilizer input and avoid over-fertilization and the subsequent loss of nutrients due to the limited sorption sites on the bone char / biochar.

Langmuir and Freundlich isotherm constants for NO3−, NH4+, PO43− and SO42

Data on Tables 4 and 5 show that the sorption behaviour of the nutrients generally conformed more to the Freundlich sorption isotherm. For all the isotherm models, the line of best fit with the greatest coefficient of determination (R^2) was adjudged as best that described the nutrients isotherm data. Several researchers have reported the preferential conformity of soil's sorption data of most nutrients to Freundlich isotherm (Azeez and Van Averbeke 2011; Azeez et al. 2014; Bankole et al. 2022). In Table 4, it was observed that the adsorption maxima (b) which indicates the number of sites for nutrient adsorption of the materials were significantly higher in the bone char than other treatments. The value of b (sulphate) in

Table 3 Slope of the isotherms at different energies of adsorption

	Energy of adsorption	Sulphate	Phosphate	Nitrate	Ammonium	Sdev. ±	mean
Soil	Lower	0.24	0.20	0.10	0.17	0.06	0.18
Soil	Higher	0.10	0.04	0.16	0.07	0.05	0.09
Animal Biochar	Lower	0.80	0.79	2.26	1.06	0.70	1.23
Animal Biochar	Higher	0.14	0.34	0.58	0.17	0.20	0.31
Plant Biochar	Lower	0.33	0.59	1.36	0.65	0.44	0.73
Plant Biochar	Higher	0.24	0.20	0.14	0.08	0.07	0.16
Soil + Animal Biochar	Lower	0.43	0.65	1.04	1.38	0.42	0.88
Soil + Animal Biochar	Higher	0.14	0.40	0.32	0.20	0.12	0.27
Soil + Plant Biochar	Lower	0.29	0.40	0.91	0.38	0.28	0.49
Soil + Plant Biochar	Higher	0.32	0.23	0.10	0.13	0.10	0.19
	Sdev.±	0.20	0.23	0.71	0.46		
	mean	0.30	0.38	0.70	0.43		

Table 4 Langmuir and Freundlich isotherm constants for sulphate and phosphate

	Sulphate						
	Langmuir constants				Freundlich constants		
	b (mg kg $^{-1}$)	K_L (L mg $^{-1}$)	MBC (L mg $^{-1}$)	R^2	K_f (L mg^{-1})	n	R^2
Soil	22.365	0.009	0.197	0.66	0.575	1.232	0.96
Animal Biochar (AB)	47.886	0.019	0.929	0.80	1.062	1.261	0.93
Plant Biochar (PB)	27.336	0.017	0.454	0.76	0.892	1.428	0.97
Soil + AB	37.759	0.021	0.810	0.94	1.086	1.407	0.98
Soil + PB	32.543	0.013	0.420	0.53	0.876	1.393	0.92
Sdev. ±	9.85	0.01	0.30		0.20	0.09	
mean	33.58	0.02	0.56		0.90	1.34	
	Phosphate						
	Langmuir constants				Freundlich constants		
	b (mg kg $^{-1}$)	K_L (L mg $^{-1}$)	MBC (L mg $^{-1}$)	R^2	K_f (L mg^{-1})	n	R^2
Soil	14.824	0.016	0.238	0.60	0.689	1.435	0.87
Animal Biochar (AB)	41.327	0.034	1.390	0.95	1.420	1.603	0.99
Plant Biochar (PB)	37.184	0.021	0.798	0.90	1.091	1.423	0.97
Soil + AB	38.400	0.021	0.794	0.77	1.101	1.426	0.96
Soil + PB	32.220	0.020	0.639	0.86	1.046	1.491	0.98
Sdev. ±	10.57	0.01	0.41		0.26	0.08	
mean	32.79	0.02	0.77		1.07	1.48	

Table 5 Langmuir and Freundlich isotherm constants for nitrate and ammonium

	Nitrate						
	Langmuir constants				Freundlich constants		
	b (mg kg $^{-1}$)	K_L (L mg $^{-1}$)	MBC (L mg $^{-1}$)	R^2	K_f (L mg^{-1})	n	R^2
Soil	-49.840	-0.002	0.120	0.11	0.413	0.992	0.95
Animal Biochar (AB)	45.263	0.061	2.745	0.88	1.833	1.777	0.91
Plant Biochar (PB)	29.607	0.070	2.074	0.99	1.609	1.864	0.91
Soil + AB	32.228	0.055	1.780	0.90	1.608	1.873	0.99
Soil + PB	26.512	0.051	1.343	0.96	1.364	1.717	0.86
Sdev.	37.91	0.03	0.98		0.56	0.37	
mean	16.75	0.05	1.61		1.37	1.64	
	Ammonium						
	Langmuir constants				Freundlich constants		
	b (mg kg $^{-1}$)	K_L (L mg $^{-1}$)	MBC (L mg $^{-1}$)	R^2	K_f (L mg^{-1})	n	R^2
Soil	10.417	0.055	0.576	0.94	1.185	2.476	0.93
Animal Biochar (AB)	37.789	0.092	3.461	0.98	2.046	2.165	0.98
Plant Biochar (PB)	31.750	0.031	0.974	0.95	1.179	1.506	0.96
Soil + AB	43.802	0.025	1.086	0.66	1.247	1.421	0.79
Soil + PB	25.550	0.027	0.700	0.89	1.162	1.713	0.96
Sdev.	12.82	0.03	1.19		0.38	0.45	
mean	29.86	0.05	1.36		1.36	1.86	

bone char was about 74% higher than that of biochar and 114% than the soil alone. This implies that bone char was richer in number of charged sites than biochar and the unamended soil for the sorption of sulphate.

Consequently, the addition of bone char led to the 69% increase in the soil adsorption maxima and 45% increase with the addition of biochar. Similarly, the binding energy (K_L) of the bone char was higher than biochar and the inclusion of either material to the soil also increased the soil binding energy. Furthermore, organic ions may raise the electrostatic attraction of phosphate in bone char, significantly raising the binding energy, as a result of an increase in the net negative surface charge brought on by nonspecific sorption. There was a corresponding increase in the sulphate buffering capacity of the soil with the addition of bone char and biochar. There is more than 300 and 200% increase in the soil sulphate buffering capacity with the addition of bone char and biochar to the soil respectively. More than 100% increase in the b parameter for phosphate sorption was recorded with the addition of either bone char or biochar to the soil. However, the ‘b’ parameter in bone char is significantly higher than the values obtained in biochar and the unamended soil. The tenacity to hold onto the adsorbed phosphate is more in the bone char than other treatments. Similar results was reported by Bankole et al. (2022).

The phosphate maximum buffering capacity of bone char is highest, followed by biochar, then soil+biochar, then soil+biochar and least in unamended soil. The buffering capacity of the materials is a measure of the ability of the soil / biochar / bone char to maintain the equilibrium nutrient concentration in the medium. It ensures the constant supply of the nutrients from the labile pool after removal by extraneous factors like erosion, leaching or plant uptake. This actually shows that the addition of either bone char or biochar improves the soil sorption sites and the sorption energy. This effect is more pronounced with the addition of bone char. The pattern observed for the Freundlich constants for both nutrients are similar to those of the Langmuir constants. For both nutrients (Table 4), the parameter (K_F) which indicates the Freundlich adsorption capacity is higher in the bone char, followed by biochar and least in the unamended soil. It was also observed that the parameter was significantly increased with the addition of the bone/biochar to the soil. Similarly, the parameter ‘n’ characterizes the heterogeneity of the system reflecting adsorption intensity (binding energy), this had the same trend as the K_F. It thus shows that bone char is more heterogeneous in its adsorption sites than biochar and the heterogeneity of the soil in significantly increased with the addition of bone char or biochar. This is most likely the result of these nutrients occupying some high-affinity binding sites, forcing more phosphate to sorb onto lower-affinity sites in bone char and changing the sorption’s character to one that is more heterogeneous. This implies that sorption binding energy is adsorbent specific and not adsorbate.

The data on Table 5 shows that the constants for nitrate sorption is similar to those of sulphate and phosphate reported earlier. Bone char had the highest Langmuir constants ‘b’ and ‘K_L’ and the MBC. The order of the constants is: bone char > biochar > soil + bone char > soil + biochar > unamended soil. The Freundlich constants had the same trend. The constant for ammonium sorption was a bit different from the trend observed for the anions. There is an inconsistent trend observed in the Langmuir constants. The ‘b’ constant observed in the bone char and biochar are higher than that of the unamended soil but the values from the soil amended with bone char had the highest ‘b’ value. The order of the ‘K_L’ is: bone char > unamended soil > biochar > soil + biochar > soil + bone char. The same pattern was observed in the Freundlich constants K_F and n. However, the bone char still had higher values than other treatments. Tamungang et al. (2016), Wang and Liang (2014) have all reported that the higher the binding energy (K_L), the higher the amount of nutrient fixed. Also, higher binding energy is a result of fewer nutrients and more sorption sites. The erratic pattern observed for ammonium might be due to its different (positive) charge compared with the negative charges of the other nutrients. Ammonium will be sorbed on negatively charged sites on the soil and bone char / biochar while nitrates, sulphate and phosphate will be sorbed on positively charged sites or through ligand exchange, independent of electrostatic attraction. Most soil colloidal sites are characterized with more of negative charges than positive charges.

The superiority of bone char over biochar might be a reflection of the significantly higher surface area in bone char over that of biochar. Biochar typically, could have as low as 8 $m^2\ g^{-1}$ surface area, but can be higher under optimal production conditions (Leng et al. 2021). Pristine biochar has been reported to contain a certain amount of surface functional groups like C–O, C═O, and −OH (Inyang et al. 2011; Uchimiya et al. 2011). Also, many studies have indicated that these functional groups on the biochar surface are responsible for contaminant removal, such as heavy metals and organic ionic compounds. The condensed aromatic structure of biochars can have amorphous C (which dominates at lower pyrolysis temperatures), turbostratic C (formed at higher temperatures) and graphite C (Keiluweit et al. 2010; Nguyen et al. 2010). However, bone char is reported to contain calcium phosphate and often hydroxyapatite; with high surface area is around 101.79 $m^2\ g^{-1}$ and mesopores of about 6 nm (Samsami et al. 2020; Chagtmi et al. 2022). Yao et al. (2012) reported from a sorption experiment that the ability of biochar to adsorb nutrients elements is not universal but dependent on the nutrient and biochar type.

Desorption studies and nutrients retention

The relationship between the amount of NO_3^-, NH_4^+, PO_4^{3-} and SO_4^{2-} desorbed by the adsorbents and the initial amount of nutrients added during the sorption phase is shown in Fig. 3. In all the nutrients, the relationship is linear, depicting that the amount of nutrients desorbed is directly proportional to the amount added at the sorption experiment. The Figure also shows that the nutrients desorption are more sensitive at high nutrient (>20 mg L^{-1}). A similar result was reported by Johan et al. (2022) for P desorption in acid soils.

The results showed that the unamended soil that desorbed a higher percentage of applied concentrations during adsorption tended to desorb a lower quantity in desorption and vice versa. The findings suggest that desorption is a gradual process and might exhibit distinct behaviors compared to adsorption in soil. Additionally,

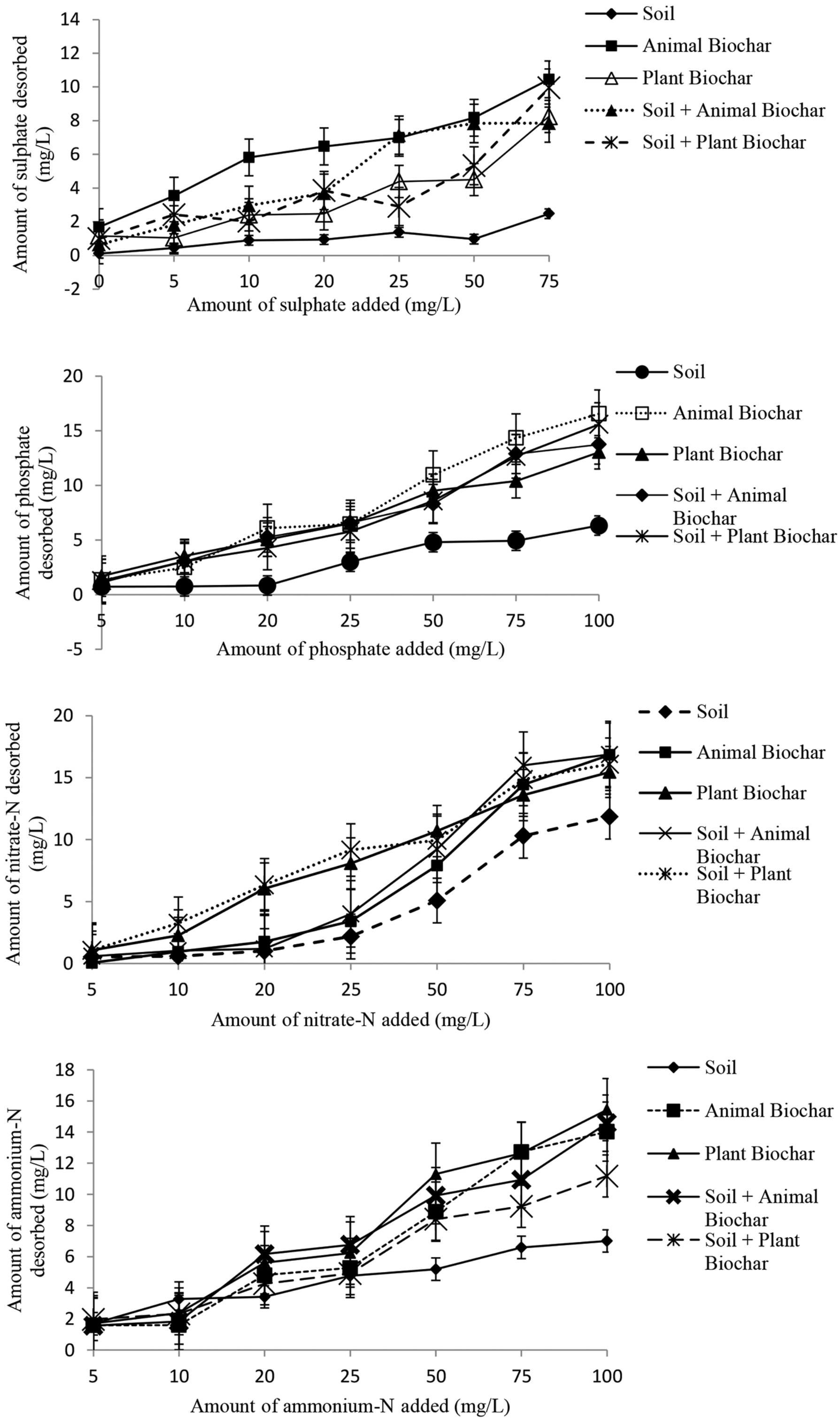

Fig. 3 Desorption of nutrient by soil, bone char, biochar and their combinations

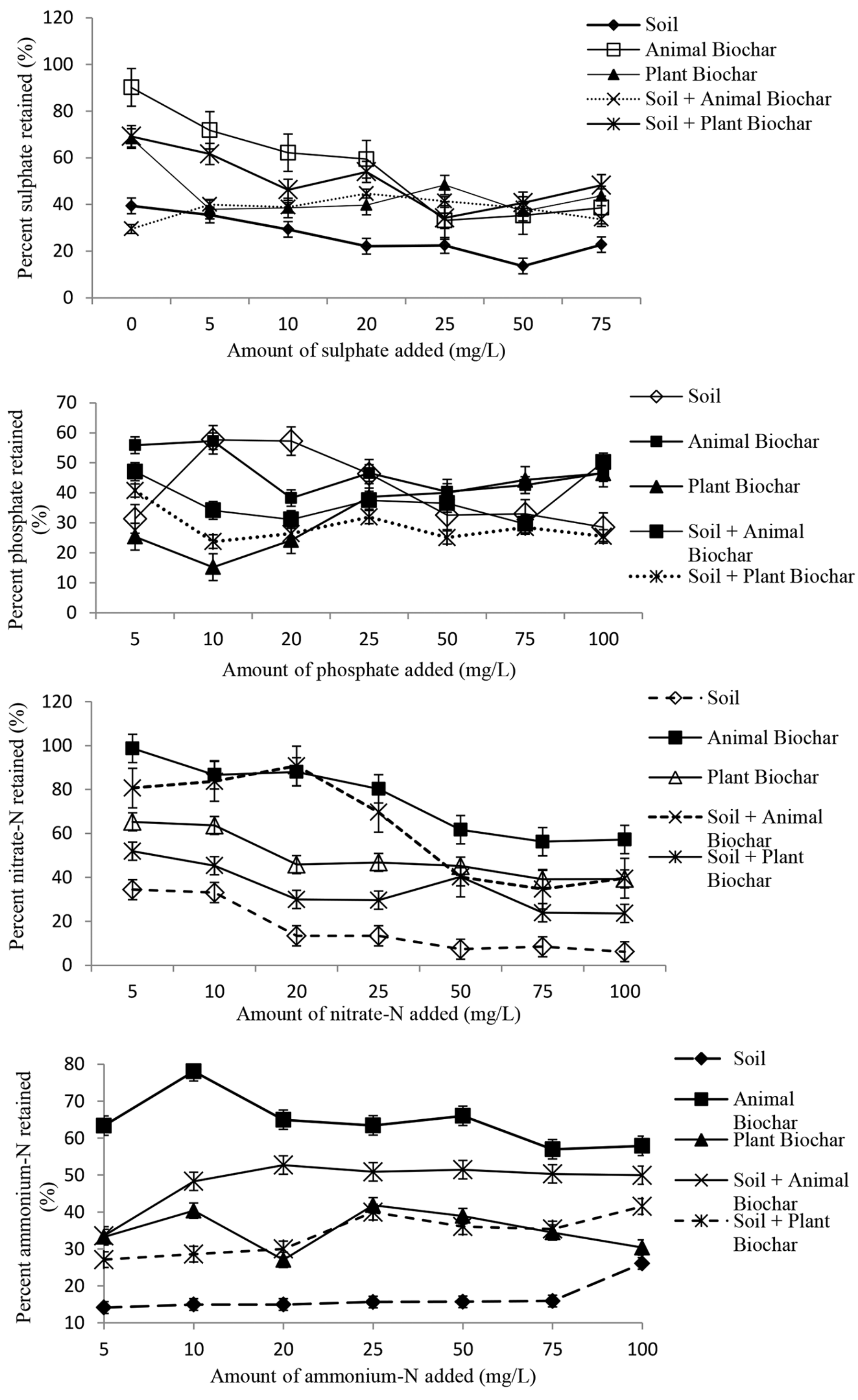

Fig. 4 Percent recoveries of sorbed nutrients

the sorption and desorption of the nutrients are inversely correlated, with the soils that adsorb P most readily releasing it in the soil solution the least.

In all the Figures it was observed that significantly, the lowest amount of nutrients was desorbed by the unamended soil. This is a reflection of the extent of the native fertility of the soil and the amount of nutrients initially sorbed at the sorption phase of the trial. The highest amount of sulphate was desorbed by the bone char while there was no clear demarcation in the amounts of desorbed phosphate, nitrate and ammonium by biochar, bone char and their mixtures with the soils. The order of nutrients desorption in the unamended soil is as follows: $NH_4^+ > NO_3^- > PO_4^{3-} > SO_4^{2-}$. Bone char and biochar desorbed more of phosphate and nitrate, respectively and least of sulphate. Generally, the soil and the amendments desorbed more nitrate, followed by ammonium, then phosphate and sulphate. The higher amounts of nitrate and ammonium desorbed might be a reflection of their high solubility in the desorptive electrolyte as this is expected from their chemical reactivity properties in terms of their position in the activity series and concentration effect of KCl 0.01 M. This further indicates that results from desorption experiment is independent of the binding energy (n) as indicated by the Freundlich n data. Thus nutrients with high n values may and may not be easily desorbed depending on the reactive components of the desorptive electrolyte. This is evident as the n values of nitrate and ammonium for bone char and biochar were though higher than the values for sulphate and phosphate, yet easily desorbed.

In order to adequately explain the proportion of the sorbed nutrients that was desorbed, the estimate of the percentage recovery of the nutrients after the desorption run is shown in Fig. 4. The unamended soil, bone char, biochar and their mixtures were observed to desorb more at lower amounts of the nutrients added. The unamended soil was observed to retain as low as 6% of added nitrate to as much as 58% of added phosphate, while on the average bone char retained 56% of added sulphate, 47% of phosphate, 76% nitrate and 64% of ammonium. The corresponding values for the biochar were 45, 33, 49, and 35%, respectively. The ability of the soil to retain added nutrients and prevent them from being desorbed was significantly increased by the addition of the bone/biochar. In all the treatments imposed it was observed that nitrate retained is highest, followed by sulphate, then ammonium and least in phosphate. For the unamended soil, phosphate is more retained while nitrate is least retained on the soil sorption sites. This trend is expected in the soil because nitrate is more easily displaced from the colloidal sites and is soluble in the soil and hence prone to leaching. However, the problem of nitrate leaching as commonly witnessed in agricultural fields could be solved by adding bone char or biochar to the soil. Similarly, the high affinity of the soil for phosphate sorption in the soil could be amended by the addition of bone char / biochar. On the average, bone char retained 60.63% of the added nutrients while biochar retained 40.68% of the nutrients. The addition of bone char led to 45.75% increase in the nutrient retention ability of the soil and 36.11% with the addition of biochar. This clearly shows that the addition of biochar or bone char alone to the soil could lead to the temporary immobilization of the soil native nutrients on the sorption sites because of nutrients retention (Lehmann et al. 2011) and hence should not be applied alone to the soil for agronomic reasons but they will only improve the soil nutrient retention ability if complementary nutrient sources as fertilizers, compost or manures are applied. Similar findings was reported by Bankole et al. (2024) and Bankole and Azeez (2024).

Conclusions

Findings from this work indicated that bone char is richer in nutrient composition than biochar made from wood shavings / sawdust, with more ability to sorb NO_3^-, NH_4^+, PO_4^{3-} and SO_4^{2-}. The bone char and biochar sorption isotherms conformed to the H-curve isotherm type, which is an indication of the strong affinity between the adsorbent (soil) and the absorbate (ions). Bone char / biochar has multiple layer adsorption sites but are finite and should be considered before being deployed as amendments for nutrient management or for environmental cleaning purposes. Hence, application of biochar for agronomic purposes needs to take cognizance of the native nutrient status of the soil so as to appropriately add the exogenous fertilizer input and avoid over-fertilization.

Both Langmuir and Freundlich sorption constants relating to adsorption maxima, binding energy and maximum nutrients buffering capacities of the soil were increased with the addition of bone char and biochar. On the average, bone char retained 60.63% of the added nutrients while biochar retained 40.68% of the nutrients. The addition of bone char led to 45.75% increase in the nutrient retention ability of the soil and 36.11% with the addition of biochar. Therefore, the nutrient sorption characteristics of a biochar should be studied prior to its use as soil nutrient amendment.

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Author contributions

Azeez J. O.: Conceptualization, Visualization, Supervision, and Original draftBankole G. O.: Investigation, Methodology, Data Curator, Formal analysis, and Project administrationAghorunse A. C.: Validation, Writing review, and editingOdelana T. B.: Validation, Writing review, and editingOguntade O. A.: Validation, Software and ResourcesAll authors reviewed the manuscript before submission.

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Data availability

The dataset used and analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests

The authors declare no competing interests.

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