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Effects of Carbonised Biomaterial Application on Nutrient and Heavy Metal Bioavailabity in Maize (*Zea Mays)* Plant

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Abstract
Many contaminants and essential soil nutrients enter plant through the soil environments and there is a drive to limit heavy metals in the soil due to their toxicity to plant and human. Bioavailable metals in contaminated soils can be remediated using green inorganic natural material such as carbonized biomaterials that have the capacity to mitigate metal availability in plant. The soil samples used for this study were obtained from open dumpsites in Benin City. Carbonized biomaterial was prepared from coconut shell. Pot experiments were carried out to assess the influence of the carbonized biomaterial on bioavailable heavy metals (Pb, Cd, As) and nutrients in maize plant. Evaluation of the carbonized biomaterial effects on the bioavailability of metals in the plant showed a gradual decrease in the concentrations of heavy metals as the rate of carbonized biomaterial increases from 0 to 40%. Assessment of carbonized biomaterial in the plant after six weeks of planting revealed increase in plant nutrients concentration as the rate of treatment increases. Therefore, the carbonized biomaterial can be used to reduce bioavailability of metals at the same time increasing the concentration of essential nutrients.

Key Words: biomaterial, maize, metals, nutrients

INTRODUCTION
Soil consists of solid phases containing organic matter and minerals phases (soil, water and air) which interact with each other. Agronomical soil releases nutrients to plants and is essential importance for degradation and transfer biomass (Brandi et *al*., 2008). A relatively small proportion of heavy metals is derived from natural process and they do not cause pollution. A much higher proportion originates from anthropogenic sources such as fertilizer and pesticide application, industrial process, domestic activities, mining, smelting and fossil fuel consumption. Heavy metals in soil from anthropogenic sources tend to be more mobile, hence more bioavailable than those from pedegenic or lithogenic sources (Okieimen and Esohe, 2014). The presence of heavy metals in soil at high concentrations may pose health hazards to human and ecosystems. Mobile bioavailable heavy metals may be reduced through complexation and adsorption with biomaterial feedstock such as carbonized biomaterial which is a popular choice derived from biological matter and which often requires little pretreatment before application to soil (Okuo and Okieimen, 2014). Addition of carbonized biomaterial to soil is increasingly receiving attention as a vital soil conditioning method for environmental and agricultural application. Carbonized material is a product of thermal conversion of biomass carried out at a temperature above 300^{o}C in the absence of air, known as pyrolysis (Duku and Hegan, 2011).

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Feedstock properties of biomaterial are different from those of uncarbonized biomass in soil (Duku and Hegan, 2011), and are known to change over time due to the weathering process; interactions with soil minerals and organic matter and oxidation by microorganisms in soil (Nguyen *et al*., 2010).

The effect of carbonized biomaterial on soil is driven by its physical and chemical properties. The difference in physical structure between carbonized biomaterial and soils lead to altered soil tensile strength, hydrodynamic and gas transport in a soil carbonized biomaterial mixture, these can be expected to have a major effects on soil biota. Carbonized biomaterials are able to complex metal ions on their surfaces making them less bioavailable which results to reduced risk of negative effects by the metal ions. However, applying carbonized biomaterial may increase the rate at which the soil solution reaches equilibrium (sorption-desorption hysteresis) (Uchimiya *et al*., 2011). This increase the rate of sorption of any other contaminants added to the soil matrix. Carbonized biomaterial has higher capacity for lead sorption than activated carbon, despite its low surface area retaining up to 6 times more lead. Due to the fact that carbonized properties gives support to soil than activated carbons (Ugbune *et al*., 2018).

The mechanisms of heavy metal removal with carbonized biomaterial amendments might be attributed to electrostatic interactions, precipitation and other reactions (Dong *et al*., 2011, Lu *et al.,* 2012). With the incorporation of biomaterial, there are major negative charges on soil surface due to the decreasing Zeta potential and increase CEC (Peng *et al*., 2011). The electrostatic attraction between heavy metal with positive charge and soil will be enhanced. The objective of this study is to investigate the effect of carbonized biomaterial derived from coconut shell on the bioavailability heavy metals and nutrients in maize plant. However, Okuo et *al*., 2014. Asai *et al.,* 2019, in their various finding asserted that carbonized material increases essential nutrient and also decrease metal contaminants in plants. In Nigeria peasant farmers used contaminated soil for farming this due to shortage of farm land occasion by increase in population and urbanization, however plant harvested from the contaminated land contained low nutrient content and high heavy metal. Currently, improved plant yield and healthy plant is limited to the use of synthetic chemicals which not well managed can cause environmental degradation and plant damaged. In addition, due to its higher cost of synthetic chemicals, farmers can no longer afford them. It becomes necessary to seek for an alternative material like carbonized biomaterial that contained nutrient, environmental friendly, easy to produce. This will increase plants nutrients and reduce heavy metals in plants.

MATERIAL AND METHODS

Sample Collection and Preparation

Soil samples for this study were obtained from Ikhueniro I(latitude 6°19'36.92"N and longitude 5°44'47.32"E), Ikhueniro II(latitude 6°19'36.92"N and longitude 5°44'47.32"E), Ugbowo (latitude 6°24'0.28"N and longitude 5°38'4.41"E) and Oluku (6°27'46.43"N and 5°36'6.77"E) open dumpsites in Benin City Edo state, Nigeria using standard methods. The coconut shell used for the carbonized biomaterial was pyrolysed in Furnace operating at 500° for 8 hours. The char produced was grinded and sieved to less than 2 mm.

Determination of Physico-chemical Properties of Soil and Coconut Shell Carbonized Biomaterial

Black method (Black, 1965) was used for pH and CEC determination. The organic carbon was determined by Nelson and Sommers (1982), Black (1965), Walkleys and Black method, (1934). The concentration of phosphorus was determined with the method of Bray and Kurtz(1947). The nitrogen content was determined by kjeldahl method. Metal concentrations was determined using Atomic Absorption Spectrophotometer (VGP 210). Level of plant nutrients (phosphorus, sodium, calcium, magnesium and potassium) were determined following standard methods (Okuo *et al.*, 2014)

Soil amendment with Carbonized Biomaterial

The coconut shell carbonized biomaterial (CSCB) was use to amend 1kg of soil (1kg of soil in plastic containers) at 4 different rates (0,5,10,20,30,40%) in triplicate, water was added and mixed frequently for 10 weeks prior to planting. The maize seeds used for this study were obtained from Delta State Ministry of Agriculture Zonal Office, Sapele. The maize plants were allowed to grow for 6 weeks then uprooted, washed thoroughly under running tap water and distilled water. Maize plants were sliced into smaller pieces. These were dried for 2 days at 80°C for 3hours before ashing in furnace. The ashes were dissolved in 20% nitric acid and filtered.

RESULTS AND DISCUSSION

Results of the physico-chemical properties of coconut shell carbonized biomaterial (CSCB) is shown in Table 1

Table 1: Physico-chemical Properties of Coconut Shell Carbonized Biomaterial

Parameter	CSCB
Moisture (%)	19.26 ±9.26
pH	9.20 ±0.20
EC (sm/cm)	2.35 ±0.35
Ash (%)	6.60 ±0.60
C (%)	85. 79 ±5. 79
N (%)	0.18 ±0.00
P (%)	0.15 ±0.01
K (%)	0.19 ±0.01
Na (%)	0.12 ±0.02
Ca (%)	11.50 ±0.01
Mg (%)	4.15 ±.15)
Pb (ppm)	< 0.01
Cd (ppm)	< 0.01
As (ppm)	<0.01

The CSCB revealed high pH, carbonized biomaterial with high pH has been shown to alter to soil pH and increases soil macro-nutrients (N, K ,Na, Ca, Mg) (Ugbune and Okuo, 2014).These essential nutrients is needed for plant growth and therefore represent valuable resources in the soil food web. Metal concentration of CSCB is quite low (<0.01). The low metal concentration of CSCB (Table 1) used in this study is an indication of soil conditioner for metal remediation in contaminated soil.

Physiochemical Properties of Dumpsite Soil Samples

Physiochemical properties of dumpsites soil results is depicted in Table 2. Soil texture of open dump sites soil showed a greater percentage of sand fraction, followed by clay (Table 2).

Table 2: Physiochemical Properties of Dumpsite Soil Samples

Parameter	Control	Sample 1	Sample 2	Sample 3	Sample 4
pH	6.71±0.01	7.02 ±0.02	7.40 ±0.40	7.52 ±0.52	7.68 ±0.68
EC(ms/cm)	0.01 ±0.01	2.4 ±0.40	7.52 ± 0.01	18.05 ±8.05	18.05 ±8.05
C (%)	0.58 ±0.58	3.27 ±0.27	3.42 ±0.42	3.22 ±0.22	3.32 ±0.32
N (%)	0.48 ±0.48	0.20 ±0.20	0.24 ±0.04	0.12 ±0.12	0.12 ±0.12
Na (meq/100g)	0.12 ±0.12	0.11 ±0.01	0.11 ±0.01	0.05±0.05	0.11 ±0.01
P (ppm)	10.24 ±0.24	112.41±1.41	75.42 ±5.42	153.24±5. 24	75.22 ±5.22
K(meg/ 100g)	0.21 ±0.21	0.23 ±0.23	0.33 ±0.33	0.19 ±0.09	0.45 ±0.45
Ca (meg/100g)	0.84 ±0.84	7.20 ±0.20	7.28 ±0.28	5.98 ±0.98	6.28 ±0.28
Mg (meg/100g)	0.22 ±0.22	2.79 ±0.79	2.36 ±0.36	2.39 ±0.39	2.98 ±0.98
Pb (ppm)	< 0.08	10.57 ±0.57	8.46 ±0.46	7.23 ±0.23	9.27 ±0.27
Cd (ppm)	< 0.01	1.75 ± 0.15	13.67 ±3.67	1.23 ±0.23	2.17 ±0.17
As (ppm)	0.30±.30	5.27 ±0.27	4.30 ±4.30	3.57 ±0.57	2.83 ±0.83
Sand (%)	78.32 ±8.32	75.96±5.96	72.54 ±2.54	74. 62 ±4. 62	77.56 ±7.56
Silt (%)	2.22 ±0.22	2.20 ±0.20	2.32±0.32	2.24 ±0.24	2.22 ±0.22
Clay (%)	19.46±9.46	21.84±1.84	25.14±5. 14	23.14 ± 0.14	20.22±0.22

High percentage of sand fraction described the soil as sandy loam. The textural analysis of soil suggest a high level of organic material in the dump sites. However, large portion of clay in dump sites soils suggest that the soil may percolate poorly with the potential harmful impact of retaining toxic metals on environmental receptors. Metal concentrations in dumpsite soil is fairly high which is a symptom of industrial wastes in the dumpsite. Level of macro-nutrients in the parent soil is also high except nitrogen, this is an evidence of organic material in the dump sites.

The pH of parent soil was found to be moderately neutral to alkaline region (6.7±0.00-7.68±0.05). pH influences availability and toxicity of heavy metal ion in soils, numerous heavy metal tend to be less mobile in soils with alkaline pH as they form insoluble complexes. The pH results of the soil samples are within the pH range of agronomical soil (Ugbune and Okuo, 2019.,Ugbune *et al.*, 2020., Ugbune *et al.*, 2021). Soil pH plays a major function in the sorption of heavy metals as it influences the solubility and hydrolysis of metal hydroxide, carbonates and phopsphate (Okieimen and Esohe, 2014). Nutrient in the study soil is moderately higher, this is an indication of the availability of domestic waste in the open dumpsite. Heavy metal concentrations in the study soils also revealed higher metal concentrations, alluding the presence of medical and industrial waste in the dump sites (Ugbune and Okuo, 2019).

Levels of Heavy Metals in Plant after Six Weeks Planting

Heavy metal level in plant grown in amended soil after six weeks planting was found to be lower than the plant grown on control soil sample (Table 3),

Table 3: Heavy Metals Concentrations in Maize Plant after 6 Weeks Planting

Sites	Parameter	0%	5%	10%	20%	30%	40%
1	Pb(ppm)	1.36± 0.02	0.97 ± 0.06	0.5 ±0.06	0.10 ±0.10	0.00 ±0.00	0.00 ±0.00
	Cd (ppm)	0.93±0.03	0.63±0.03	0.10±0.00	0.00 ±0.00	0.00 ±0.00	0.00 ±0.00
	As (ppm)	1.07±0.07	0.70 ±0.00	0.33±0.06	0.00 ±0.00	0.00 ±0.00	0.00±0.00
2	Pb (ppm)	1.50±0.50	1.23 ±0.23	0.40 ± 0.00	0.10±0.00	0.00 ±0.00	0.00 ±0.00
	Cd (ppm)	0.93±0.08	0.63 ±0.03	0.10±0.00	0.00 ±0.00	0.00 ±0.00	0.00±0.00
	As (ppm)	0.97±0.03	0.43±0.02	0.10±0.02	0.00±0.00	0.00 ±0.00	0.00±0.00
3	Pb (ppm)	1.00±0.04	0.73±0.03	0.33 ±0.02	0.00±0.00	0.00 ±0.00	0.00 ±0.00
	Cd (ppm)	0.30±0.00	0.10 ±0.00	0.00 ±0.00	0.00±0.00	0.00 ±0.00	0.00±0.00
	As (ppm)	0.97±0.05	0.43 ±0.02	0.43±0.03	0.10±0.00	0.00 ±0.00	0.00±0.00
4	Pb (ppm)	0.63±0.04	0.23±0.03	0.00 ±0.00	0.00±0.00	000 ± 0.00	0.00±0.00
	Cd (ppm)	0.27±0.03	0.00±0.00	0.00 ±0.00	0.00±0.00	0.00±0.00	0.00±0.00
	As (ppm)	0.33±0.40	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00

this is an indication that plant in treated soil with CSCB reduces in metal concentration as the rate of amendment increases, this revealed that the metals undergo complexation and precipitation by CSCB in soil, marking the metals unavailable for plant uptake (Ugbune *et al.*, 2018).This is due to the increase in pH and CEC as a result of CSCB released to the soil environment .The lowest metal plant uptake was for maize planted with 40% CSCB while the highest metal plant absorption was for plant applied with 5% CSCB.

Level of Nutrient in Maize Plant after Six Weeks of Planting

The results of maize plant after CSCB treatment (Table 5) revealed greater levels of plant nutrients than those harvested from soil without carbonized biomaterial treatment.

Table 4: Nutrient levels of plant (maize) after 6 weeks planting

Sites	Parameter	0%	5%	10%	20%	30%	40%
1	N(%)	0.16 ± 0.04	0.19 ± 0.02	0.28 ± 0.04	0.33 ± 0.03	0.40 ± 0.05	0.46 ± 0.04
	P (ppm)	18.6± 0.78	43.27 ± 3.18	64.17± 7.76	68.90± 5.29	77.13 ± 2.56	83.80 ± 1.73
	K (%)	0.30 ±0.00	033 ± 0.01	0.40 ± 0.00	0.41 ± 0.00	0.46 ± 0.02	0.60 ± 0.08
	Na (%)	0.09 ± 0.00	0.10 ± 0.01	0.12 ± 0.01	0.13 ± 0.01	0.14 ± 0.00	0.15 ± 0.02
	Ca (%)	0.25 ± 0.25	0.30 ± 0.02	0.42 ± 0.09	0.47 ± 0.09	0.53 ± 0.10	0.61 ± 0.09
	Mg (%)	0.11 ± 0.02	0.14 ± 0.03	0.20 ± 0.12	0.28 ± 0.12	0.35 ± 0.09	0.42 ± 0.05
2	N(%)	0.25 ± 0.02	0.26 ±0. 02	0.30 ± 0.02	0.36 ± 0.03	0.41 ± 0.20	0.46 ± 0.89
	P (ppm)	12.4± 0.93	12.57± 0.75	22.20± 1.08	35.07± 0.81	38.47 ± 0.49	44.90 ± 0.89
	K (%)	0.17 ± 0.06	0.20 ± 0.00	0.31 ± 0.02	0.39 ± 0.02	0.4 ± 0.01	0.57 ± 0.05
	Na (%)	0.10 ± 0.00	0.10 ± 0.00	0.12 ± 0.01	0.14 ± 0.00	0.16 ± 0.01	0.19 ± 0.01
	Ca (%)	0.21 ± 0.02	0.21 ± 0.02	0.25 ± 0.01	0.35 ± 0.03	0.51 ± 0.04	0. 67 ± 0.04
	Mg (%)	0.12 ±0.03	0.13 ± 0.02	0.21 ± 0.02	0.23 ± 0.03	0.33 ± 0.04	0.43 ± 0.02
3	N(%)	0.13 ± 0.02	0.15 ± 0.02	0.20 ± 0.02	0.23 ± 0.03	0.40 ± 0.02	0.52 ± 0.03
	P (ppm)	12.67± 0.93	14.33 ± 0.47	16 .93 ± 0.57	19.20 ± 0.26	25.70± 0.61	41.80± 2.65
	K (%)	0.20 ± 0.00	0.21 ± 0.02	0.28 ± 0.03	0.30 ± 0.00	0.40 ± 0.02	0.61 ± 0.04
	Na (%)	0.10 ± 0.00	0.10 ± 0.01	0.12 ± 0.00	0.14 ± 0.00	0.17 ± 0.01	0.20 ± 0.00
	Ca (%)	0.21 ± 0.02	0.26 ± 0.03	0.40 ± 0.03	0.44 ± 0.08	0.54 ± 0.04	0.69 ± 0.03
	Mg (%)	0.12 ± 0.03	0.15 ± 0.10	0.21 ± 0.02	0.30 ± 0.04	0.36 ± 0.02	0.48 ± 0.03
4	N(%)	0.09 ± 0.01	0.12 ± 0.01	0.13 ± 0.02	0.18 ± 0.02	0.30 ± 0.02	0.48 ± 9.92
	P (ppm)	10.23 ± 0.38	12.73 ± 1.23	20.47 ± 0.73	25. 13± 0.37	25.13 ± 0.37	33.07± 0.35
	K (%)	0.12 ± 0.02	0.14 ± 0.02	0.22 ± 0.02	0.32 ± 0.01	0.32 ± 0.01	0.47 ± 0.03
	Na (%)	0.07 ± 0.01	0.09 ± 0.01	0.14 ± 0.02	0.20 ± 0.00	0.20 ± 0.0	0.26 ± 0.03
	Ca (%)	0.21 ± 0.04	0.22 ± 0.02	0.33 ± 0.06	0.53 ± 0.02	0.53 ± 0.02	0.67 ± 0.02
	Mg (%)	0.11 ± 0.02	0.12 ± 0.02	0.15 ± 0.03	0.31 ± 0.03	0.31 ± 0.03	0.47 ± 0.03

This is due to the uptake of nutrient by the plant as a result of the released of more nutrients by CSCB into the soil solution. Plants planted with 40% CSCB had the highest nutrient concentrations while the plant planted with 5% had the least. An earlier work by (Okuo *et al*., 2014) gave similar results.

CONCLUSION

Carbonized biomaterial used for this study contained high quantities of nutrient and extremely low heavy metal. On the other hand, parent soil contained low nutrient and very high heavy metal. Results obtained from plant harvested from plant grown on amended soil show decrease in metal concentration as the rate of amendment increases from 0 to 40%.The research also revealed that plant obtained from treated soil show increase in plant essential nutrient as the percentage of amendment increases. Therefore, this study has demonstrated that coconut shell carbonized biomaterial can be used to reduce heavy metal and increase essential plant nutrient for the health benefit of mankind.

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