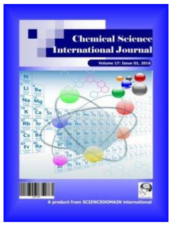

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Impact of Carbonised Briquette on the Fractionation of Trace Metals in Dumpsite Soils

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

Increase in domestic and industrial waste increases the concentration of trace metals in dumpsites soil. The level of trace metal concentration of dumpsite soil needs to be analysed for proper metal contamination management. Soil metal contamination can be managed using organic material such as carbonised sawdust. In this study, soil samples were collected from selected dumpsites in Benin City, using standard method.

Carbonised briquette was prepared from softwood sawdust obtained Carbonised briquette was prepared from softwood sawdust obtained from a sawmill in Sapele Town. The effects of carbonised briquette on metal fractionation were investigated using standard method. Fraction studies revealed that carbonised briquette the amendment results in the decrease in the levels of Zn, Cu, Mn and Cr in the different fractions. The decrease follows the order: exchangeable < carbonate < Fe-Mn oxide < organic < residual. Suggesting reduction in mobility and bioavailability of the metals after carbonised briquette amendment.

Therefore, this study revealed that carbonised briquette can be used to immobilise metals and also as a medium to manage trace metals soil contamination.

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Keywords: Soil fractionation; carbonised briquette; dumpsite soil.

1. INTRODUCTION

Trace metals occur naturally in the ecosystem with large variations in concentrations [1]. The presence of trace metals in the environment is of great ecological significance due to their toxicity of certain concentration, translocation through food chains and non- biodegradability which is responsible for their accumulation in the biosphere [2], these metals are undergoing global ecological circle [2]. Toxic metals availability to biota can change considerably depending on their chemical speciation in the soil. The mobility of these metalsspecies may be increased over time as the waste becomes more acidic and oxidizing conditions dominate [3]. The buildup of metal species in the environment such as dumpsite soils is attributed to industrial and domestic waste. Knowledge of dumpsite soil ecological health is critical to sustaining soil contamination management using organically amended such as carbonised feedstock.

Carbonised feedstock a byproduct of the pyrolysis process, is biomass-derived black carbon intended for use as a soil amendment. It is analogous to charcoal manufactured through traditional or modern pyrolysis methods, and to black carbon found naturally in ecosystems.

The type of organic matter (Feedstock) that is used and the condition under which a carbonised feedstock is produced greatly affects its relative quality as a soil amendment [4,5]. The most important measures of carbonised feedstock quality appears to be high absorption, cation exchange capacities and low level of mobile metal such as trace metals [6,7,4,5]. The microscopic physical structure of carbonised feedstock is thekey to its success in reducing heavy contamination [8]. Hossain et al. [9], reported that carbonised feedstock can induce and increase the metal fraction of soil and decrease trace metal uptake in the soil. Carbonised feedstock application reduce the extractability of heavy metals such as cadmium from the soil. This significant change in the extractability and in the metal sequential fractionation indicated that the available exchange a form of trace metal in the soil can be transformed into an unexchangeable form [10].

Carbonised feedstock has a higher sorption affinity for a range of organic and inorganic compounds and higher nutrient retention ability compared to other forms of soil organic matter [11,12,13,14]. Once carbonised feedstock added to the soil, abiotic and biotic surface oxidation occur. The increased surface carboxyl groups, a greater negative charge, and subsequently an increasing ability to sorb cations [15,16]. It also exhibits an ability to sorb polar compounds including many environmental contaminants [17]. Cation exchange capacity of carbonised feedstock is highly variable depending upon the pyrolysis conditions under which it is produced.

Carbonised feedstock properties may enhance soil microbial communities and create microenvironments that encourage microbial colonisation. Hence the objectives of this study where to access the effect of carbonised briquette on trace metals fractionation of Zn, Cu, Mn and Cr in dumpsites soil.

2. MATERIALS AND METHODS

2.1 Collection and Preparation of Soil Sample

Soil samples were collected from four dumpsites in Benin City (latitude 6° 47[1] and 7° 15[1] and Longitude 5° 49[1] and 6° 14[1]), Nigeria (Fig. 1), namely Upper Ekenwan Road (1); Darlington Avenue off Akpobor street, Oriokpa Quarters, G.R.A, Benin City (2); Ikhenero I (3) and Ikhenero II (4). In the laboratory, the soils were dried at ambient temperature (28°C), crushed in a porcelain mortar and sieved through 2 mm stainless sieve. Samples were stored in a polythene bag and properly labelled for subsequent analysis.

2.2 Carbonised Briquette Production

Softwood sawdust was collected from a sawmill in Sapele town, Delta State, Nigeria. Carbonised briquette production was done according to the method described by [18]. Metal concentration was determined using AAS (VGP 2010 model).

2.3 Determination of Physical Properties of Carbonised Briquette

The pH was determined following the method of [19] while electrical conductivity. (EC) was determine using [20].

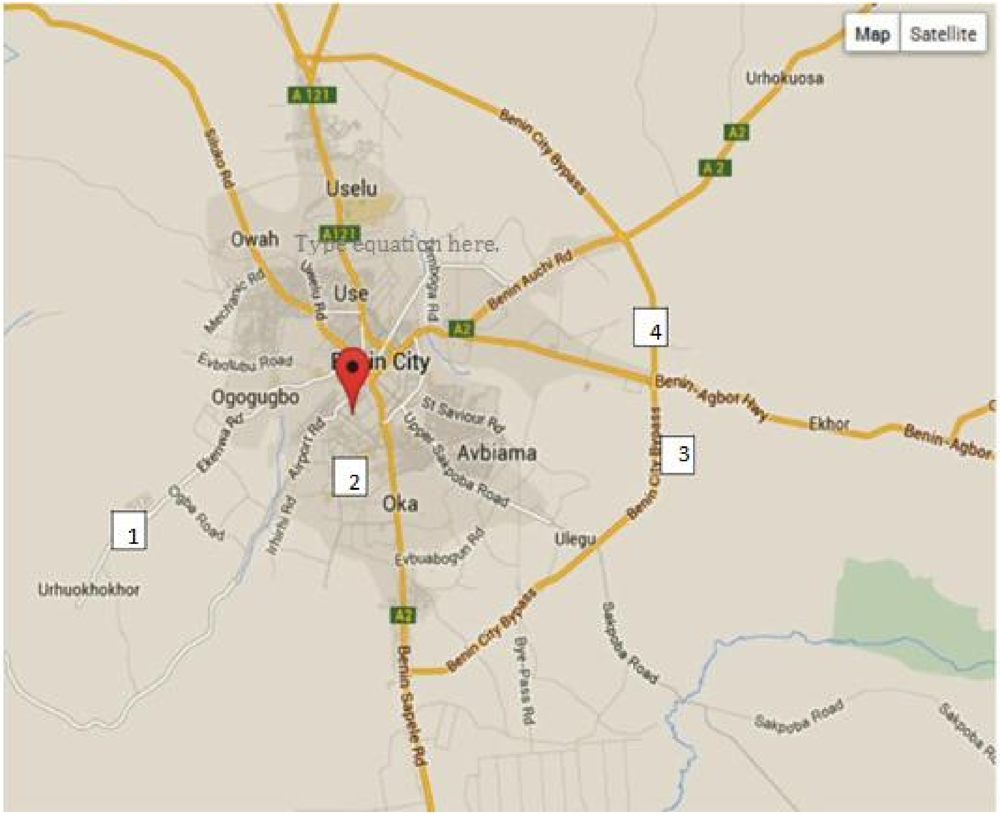

Fig. 1. Benin city map showing sampling locations

2.4 Pot Experiment

1 Kg of the thoroughly mixed soil from dumpsite containing 0, 5, 10, 20, 30 and 40% of carbonised briquette were placed in 6 plastic pots for each dumpsite. They were mixed thoroughly, watered with 10 ml of deionised water and stirred twice a week for 10 weeks for stabilisation to take place. These were kept in the greenhouse before analysis.

2.5 Fractionation of Trace Metals in Soil

In this study, fractionation of metal in soil was assessed using sequential extraction procedures according to Tessiers Scheme [21]. This was done after 10 weeks Stabilisation period with carbonised sawdust amendment.

3. RESULTS AND DISCUSSION

The result of physical properties of carbonised briquette (Table 1) revealed that is a potential amender for the management of metal contaminated soil. Thus, high pH and moderate EC is a the parameter for trace metal complexation.

Table 1. Physical properties of carbonised briquette

Parameter	Carbonized briquette
pH	9.24±0.18
EC(Ms/cm)	2.42±00

3.1 Effects of Carbonised Briquette on the Fractionation of Soil and Amended Soil for Heavy Metals

Results of fractionation of parent and amended soil (Tables 2 – 5) show a reduction in the amount of Zn, Cu, Mn and Cr in the exchangeable and carbonate pool. The decrease in exchangeable and carbonate pool could be attributed to carbonised briquette application that raises soil pH thereby promoting the precipitation of metals. The results are consistent with those of [22,23], which showed that when the soil pH was changed as a result of carbonised feedstock application, Cd and Zn were redistributed between exchangeable and carbonate forms while other fractions were almost unchanged. Previous studies of [24-27], suggested that the conversion of the exchangeable form of heavy metal to less available organic the bound metal via complexation reactions can be attributed to the significant reduction of extractable metals in carbonised feedstock amended the soil. Trace metals in the exchangeable phase (Zn, Cu, Mn, and Cr) decreases, leading to decrease in its bioavailability and mobility of the studied soil.

Table 2. Concentration (ppm) of Zn in various geochemical fractions of the soil and rate of amendments

Sites	Fraction	0%	5%	10%	20%	30%	40%
1	Exchangeable	2.70±0.10	1.83±0.12	1.53±0.12	1.23±0.12	0.67±0.06	0.37±0.06
	Carbonate	5.57±0.12	3.97±0.12	3.83±0.06	3.46±0.06	2.77±0.15	2.13±0.06
	Fe-Mn oxide	5.67±0.12	5.17±0.12	5.33±0.15	5.63±0.06	6.03±0.12	5.90±0.10
	Organic	5.73±0.15	6.13±0.63	6.63±0.06	6.76±0.06	7.73±0.15	7.73±0.06
	Residual	7.70±0.06	10.47±0.63	10.47±0.06	10.77±0.12	11.10±0.10	11.80±0.00
	Sum of fraction	27.37±0.55	27.57±0.99	27.80±0.45	27.87±0.42	27.90±0.58	27.93±0.28
2	Exchangeable	3.9±30.15	3.33±0.06	2.37±0.12	1.83±0.15	0.97±0.15	0.23±0.06
	Carbonate	5.43±0.15	4.77±0.15	4.27±0.06	3.73±0.15	24.3±0.21	1.47±0.06
	Fe-Mn oxide	6.83±0.12	7.00±0.10	7.20±0.10	7.83±0.12	8.57±0.15	8.73±0.15
	Organic	7.54±0.06	7.73±0.15	8.27±0.12	8.53±0.15	9.17±0.15	9.63±0.06
	Residual	8.07±0.15	9.06±0.15	10.03±0.15	10.73±0.15	11.73±0.21	13.49±0.21
	Sum of fraction	31.83±0.63	31.93±0.61	32.14±0.55	32.64±0.72	32.87±0.89	33.49±0.57
3	Exchangeable	6.37±0.15	5.23±0.15	3.87±0.15	2.53±0.15	1.43±0.12	0.37±0.12
	Carbonate	7.63±0.12	6.47±0.21	5.53±0.12	4.37±0.06	2.27±0.07	1.57±0.12
	Fe-Mn oxide	8.42±0.17	8.80±0.12	9.83±0.06	10.74±0.06	12.49±0.06	13.23±0.21
	Organic	9.53±0.12	10.130.15	11.27±0.17	12.43±0.15	14.180.12	14.61±0.15
	Residual	10.67±0.32	12.00±0.27	13.03±0.21	14.540.12	15.160.06	16.19±0.15
	Sum of fraction	42.60±0.88	42.63±0.90	43.53±0.71	44.610.54	45.530.43	45.97±0.75
4	Exchangeable	3.37±0.12	2.93±0.15	1.47±0.15	1.17±0.12	0.37±0.06	0.10±0.00
	Carbonate	4.97±0.12	4.37±0.06	3.17±0.12	2.87±0.06	1.57±0.15	0.73±0.15
	Fe-Mn oxide	8.73±0.15	9.33±0.06	9.53±0.12	9.67±0.15	10.37±0.06	10.54±0.15
	Organic	9.29±0.15	9.97±0.12	11.00±0.26	11.07±0.15	11.63±0.15	11.87±0.06
	Residual	10.27±0.15	11.10±0.06	12.60±0.06	13.02±0.15	14.00±0.06	14.83±0.06
	Sum of fraction	36.63±0.69	37.70±0.45	37.77±0.71	37.80±0.63	37.93±0.54	38.07±0.45

Table 3. Concentration (ppm) of cu in various geochemical fractions of the soil and the rate of amendments

Sites	Fraction	0%	5%	10%	20%	30%	40%
1	Exchangeable	1.67±0.06	1.53±0.12	1.46±0.15	1.32±0.06	1.27±0.06	0.37±0.06
	Carbonate	3.23±0.12	2.73±0.15	2.43±0.15	2.40±0.15	2.33±0.06	2.27±0.12
	Fe-Mn oxide	4.87±0.06	5.43±0.06	5.44±0.06	5.45±0.15	5.47±0.15	6.33±0.06
	Organic	5.830.06	6.430.15	6.450.23	6.47+_0.22	6.60+_0.00	6.70+_0.10
	Residual	6.730.15	6.930.06	8.430.12	8.76+_0.12	8.87+_0.12	9.53+_0.15
	Sum of fraction	22.33±0.45	23.05±0.45	24.21±0.71	24.40±0.70	24.54±0.33	25.20±0.49
2	Exchangeable	2.07±0.06	1.37±0.06	1.07±0.06	0.57±0.15	0.27±0.12	0.00±0.00
	Carbonate	3.33±0.06	2.47±0.15	1.83±0.15	1.27±0.15	1.07±0.06	0.57±0.06
	Fe-Mn oxide	4.03±0.15	5.03±0.15	5.03±0.06	4.93±0.15	5.17±0.06	5.37±0.15
	Organic	4.22±0.15	5.13±0.15	5.13±0.06	5.43±0.15	5.93±0.06	6.43±0.15
	Residual	4.97±0.15	5.27±0.15	6.37±0.06	7.37±0.15	7.53±0.15	8.40±0.15
	Sum of fraction	18.62±0.57	19.27±0.66	19.43±0.39	19.57±0.76	19.97±0.45	20.80±0.51
3	Exchangeable	2.17±0.06	1.67±0.15	1.07±0.06	0.60±0.20	0.13±0.12	0.07±0.06
	Carbonate	3.97±0.15	3.73±0.15	2.37±0.06	1.67±0.15	1.03±0.06	0.33±0.06
	Fe-Mn oxide	5.17±0.38	5.24±0.17	5.63±0.06	6.57±0.23	6.89±0.06	6.90±0.00
	Organic	5.27±0.06	5.52±0.06	6.53±0.15	6.78±0.12	6.97±0.06	7.57±0.15
	Residual	5.30±0.10	6.17±0.15	6.77±0.15	6.83±0.06	7.53±0.15	8.12±0.15
	Sum of fraction	21.88±0.75	22.33±0.68	22.37±0.48	22.45±0.76	22.55±0.48	22.99±0.42
4	Exchangeable	2.23±0.15	1.73±0.15	0.93±0.06	0.33±0.06	0.10±0.00	0.07±0.06
	Carbonate	4.57±0.15	3.83±0.06	2.40±0.17	2.17±0.06	1.13±0.12	0.73±0.06
	Fe-Mn oxide	5.13±0.06	5.34±0.21	6.73±0.06	6.93±0.10	6.97±0.12	7.03±0.06
	Organic	5.83±0.06	6.73±0.12	6.87±0.15	7.40±0.10	7.64±0.15	7.73±0.12
	Residual	6.23±0.06	6.93±0.06	7.73±0.15	7.93±0.15	8.77±0.12	9.43±0.15
	Sum of fraction	23.99±0.48	24.59±0.60	24.72±0.59	24.07±0.53	24.64±0.51	24.99±0.45

Table 4. Concentration (ppm) of Mn in various geochemical fractions of the soil and rate of amendments

Sites	Fractions	0%	5%	10%	20%	30%	40%
1	Exchangeable	1.13±0.06	0.73±0.12	0.63±0.06	0.43±0.06	0.33±0.06	0.10±0.06
	Carbonate	1.43±0.06	1.27±0.06	1.33±0.06	1.13±0.06	0.930.06	0.63±0.06
	Fe-Mn oxide	1.67±0.06	1.83±0.12	2.33±0.06	2.37±0.06	2.47±0.06	2.73±0.06
	Organic	2.08±0.06	2.43±0.15	2.53±0.12	3.07±0.15	3.17±0.12	4.54±0.15
	Residual	2.76±0.12	3.53±0.21	3.41±0.12	3.57±0.15	3.77±0.15	4.54±0.15
	Sum of fraction	9.07±0.36	9.79±0.66	10.23±0.42	10.57±0.48	10.67±0.45	11.23±0.39
2	Exchangeable	0.97±0.06	0.63±0.06	0.27±0.06	0.10±0.00	0.00±0.00	0.00±0.00
	Carbonate	1.33±0.06	1.06±0.00	0.77±0.15	0.37±0.06	0.13±0.06	0.00±0.00
	Fe-Mn oxide	1.87±0.06	2.17±0.15	2.53±0.06	2.80±0.10	2.87±0.06	3.13±0.12
	Organic	2.53±0.12	2.90±0.10	3.27±0.15	3.47±0.06	3.73±0.15	3.63±0.06
	Residual	3.13±0.06	3.47±0.06	3.76±0.15	4.36±0.15	4.74±0.00	4.94±0.15
	Sum of fraction	9.83±0.36	10.09±0.43	10.60±0.57	11.43±0.30	11.47±0.42	11.70±0.38
3	Exchangeable	1.06±0.06	0.63±0.06	0.27±0.12	0.10±0.00	0.00±0.00	0.00±0.00
	Carbonate	1.63±0.06	1.07±0.06	0.40±0.06	0.33±0.06	0.13±0.06	0.00±0.00
	Fe-Mn oxide	2.26±0.06	2.43±0.06	2.83±0.15	2.86±0.06	3.03±0.06	3.33±0.06
	Organic	2.82±0.06	2.93±0.06	3.10±0.17	3.16±0.06	3.33±0.12	3.63±0.15
	Residual	3.20±0.06	4.03±0.06	4.70±0.15	4.96±0.12	5.54±0.06	6.27±0.06
	Sum of fraction	10.97±0.30	11.09±0.30	11.30±0.55	11.43±0.00	12.03±0.30	13.23±0.38
4	Exchangeable	1.03±0.12	0.57±0.06	0.23±0.06	0.07±0.06	0.07±0.00	0.01±0.00
	Carbonate	2.03±0.06	1.27±0.15	0.73±0.15	0.33±0.06	0.23±0.12	0.20±0.06
	Fe-Mn oxide	2.67±0.06	2.90±0.17	2.93±0.15	3.27±0.06	3.30±0.10	4.31±0.15
	Organic	3.47±0.06	4.06±0.12	4.17±0.06	4.33±0.06	4.30±0.10	4.31±0.15
	Residual	4.13±0.06	4.06±0.06	5.47±0.06	6.07±0.15	6.27±0.15	6.66±0.06
	Sum of fraction	13.33±0.36	13.40±0.56	13.53±0.48	14.07±0.39	14.17±0.53	14.62±0.39

3.2 Concentration (ppm) of Zn in Various Geochemical Fractions of the Soil and Amended Soil with Carbonised Briquette

Results in Tables 2 shows that the zinc in the soil and amended soil were moderately associated with Fe-Mn oxide and organic Fraction. Exchangeable fraction had the lowest percentage composition. The Fraction followed the order: residual> organic> Fe-Mn oxide> carbonate> exchangeable. The non- dominance of zinc in the first fraction indicates that zinc was not readily adsorbed on the surface of several soil constituents such, as clay mineral, organic matter and hydrous oxide, thus potentially less mobile and low bioavailability.

3.3 Concentration (ppm) of Cu in Various Geochemical Fraction of the Soil and Amended Soil with Carbonised Briquette

Fractionation results presented in Table 3 indicates that Cu was mostly found in the residual fraction of the parent soil and amended soil, followed by an organic bound fraction, Fe-Mn oxide fraction, carbonate fraction and an exchangeable fraction. The values for residual the fraction at 0% amendment has the lowest while 40% amendment gave the highest. This partition pattern indicates a less potential mobility and low bioavailability of the metal.

3.4 Concentration (ppm) of Mn in Various Geochemical Fraction of the Soil and Amended with Carbonised Briquette

Fractionation results shown in Tables 4 indicate that manganese is mostly concentrated in the last three phase. The association pattern of manganese in different phase where in the order residual> organic > Fe-Mn oxide> carbonate >exchangeable. The low abundance of Mn in the exchangeable fraction in dumpsite and amended soil indicate low mobility.

3.5 Concentration (ppm) of Cr in Various Geochemical Fraction of the Soil and Amended with Carbonised Briquette

The distribution of chromium in the studied soil is in the order: residual >organic> Fe-Mn

Table 5. Concentration (ppm) of Cr in various geochemical fractions of the soil and rate of amendments

Sites	Fractions	0%	5%	10%	20%	30%	40%
1	Exchangeable	0.63±0.06	0.33±0.06	0.20±0.00	0.00±0.00	0.00±0.00	0.00±0.00
	Carbonate	0.87±0.06	0.67±0.06	0.43±0.06	0.23±0.06	0.00±0.00	0.00±0.00
	Fe-Mn oxide	1.13±0.06	1.33±0.06	1.53±0.06	1.57±0.06	1.57±0.06	1.33±0.06
	Organic	1.27±0.12	1.43±0.06	1.83±0.06	1.83±0.06	1.97±0.06	1.77±0.06
	Residual	1.43±0.12	3.41±0.06	2.04±0.06	2.58±0.06	2.86±0.06	3.37±0.06
	Sum of fraction	5.17±0.42	0.00±0.30	5.83±0.24	6.17±0.24	6.40±0.18	6.47±0.18
2	Exchangeable	0.20±0.00	0.07±0.06	0.000.00	0.00±0.00	0.00±0.00	0.00±0.00
	Carbonate	0.43±0.06	0.17±0.06	0.10±0.10	0.00±0.00	0.00±0.00	0.00±0.00
	Fe-Mn oxide	0.53±0.06	0.77±0.15	0.77±0.06	0.77±0.06	0.73±0.06	0.73±0.06
	Organic	0.67±0.06	0.97±0.15	1.07±0.06	1.03±0.06	1.07±0.06	1.03±0.06
	Residual	1.33±0.06	1.43±0.06	1.79±0.00	1.97±0.06	2.30±0.06	2.14±0.06
	Sum of fraction	3.16±0.24	3.41±0.48	3.73±0.22	3.77±0.17	3.83±0.18	3.90±0.18
3	Exchangeable	0.10±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
	Carbonate	0.17±0.06	0.70±0.06	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
	Fe-Mn oxide	0.53±0.06	0.43±0.64	0.53±0.06	0.57±0.06	0.63±0.06	0.70±0.00
	Organic	1.03±0.06	0.93±0.12	0.97±0.06	1.06±0.06	0.17±0.06	1.83±0.12
	Residual	1.33±0.12	1.83±0.06	1.93±0.06	2.13±0.06	2.64±0.15	3.83±0.15
	Sum of fraction	3.16±0.30	3.26±0.30	3.43±0.18	3.76±0.18	4.44±0.27	6.36±0.39
4	Exchangeable	0.23±0.00	0.17±0.00	0.13±0.00	0.07±0.06	0.00±0.00	0.00±0.00
	Carbonate	0.50±0.00	0.40±0.10	0.17±0.06	0.10±0.00	0.00±0.00	0.00±0.00
	Fe-Mn oxide	0.93±0.06	0.97±0.06	1.07±0.06	1.08±0.11	1.63±0.06	1.67±0.12
	Organic	1.33±0.06	1.33±0.11	1.50±0.10	1.67±0.12	1.76±0.06	1.83±0.12
	Residual	1.78±0.06	1.93±0.06	2.16±0.06	2.36±0.15	2.83±0.15	2.96±0.15
	Sum of fraction	4.77±0.24	4.80±0.39	5.03±0.34	5.27±0.38	6.22±0.27	6.46±0.39

oxide>carbonate> exchangeable (Table 5). The distribution pattern shows a low potential mobility. Partition pattern of chromium of the study show a similar environmental behaviour like other metals of these studies.

4. CONCLUSION

Trace metal fractionation of dumpsites soil and amended with carbonised briquette revealed the distribution pattern of zinc, copper, manganese and chromium. Carbonised briquette educes soil metals in the exchangeable and carbonate pool as the rate of amendment increases. The association pattern of metals in different phase follow the following order: exchangeable < carbonates < Fe-Mn oxide < organic < residual. Therefore carbonised briquette can be used to transformed metals from mobile and bioavailable phase into less bioavailable formed in contaminated soil.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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