

FRACTIONATION OF LEAD AND CADMIUM IN REFUSE DUMP SOIL TREATED WITH CASSAVA MILL EFFLUENT

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ABSTRACT

The effect of application of cassava (Manihot esculenta) processing mill effluent (CME) on the chemical fractionation of lead (Pb) and cadmium (Cd) in soil obtained from a refuse dump site was assessed in this study. Selected physicochemical properties of the soil and CME were determined while four different amounts of the CME were applied to the soil. The refuse dump soil had average pH of 6.2, while the cation exchange capacity was dominated by calcium. Similarly, the CME had a mean pH of 4.21 and high mean phosphorus concentration of 3160mg/kg. Chemical fractionation of the soil not containing CME showed 58.65 and 7.90mg/kg of Pb and Cd respectively in the carbonate fraction. Following the application of CME, there was redistribution of Pb and Cd in the different fractions. CME contributed to increase Cd amount in the carbonate fraction, while the residual fraction had almost uniform distribution of Cd with the various treatments of CME. However, the result indicated that depending on the applied amount of the CME there was an overall reduction in the concentration of Pb in the different fraction, while there were corresponding increases for Cd amongst the various fractions in the soil.

Key words: Chemical fractionation, lead, cadmium, dump soil, cassava mill-effluent, cation exchange.

INTRODUCTION

The application of biosolids, sludge, effluents, and other processing wastes on land is an age long practice. Furthermore, the interest in spreading sewage sludge from municipal sewage treatment plants on agricultural and forested land as a nutrient subsidy is steadily increasing (Tomlin *et al.*, 1993). The use of biosolids and effluents from process industry in cropland and forestland may be restricted by their heavy metal contents. Heavy metals most commonly found in biosolids are lead, nickel, cadmium, chromium, copper and zinc, and the metal concentrations are governed by the nature and the intensity of the industrial activity as well as the type of process employed during the bio solid treatment (Wang, *et al.*, 2003).

While there abound numerous reports on the effect of the application of bio-solids and effluents with high heavy metal loadings on soil heavy metal concentration and plant uptake, there is a dearth of works on the effect or consequences of the application of these substances on the metal concentrations of soils. The availability, distribution and dynamics of heavy metals in soil is determined by both soil physicochemical properties and the forms or fractions of occurrence of these metals in soils. Consequently, the nature, type and physicochemical properties of the bio-solids will no doubt have profound effect on the mobility of the metals in soils, especially in soils pressured to having high heavy metal loads.

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A large proportion of harvested cassava roots are processed into food, animal feed and various industrial products. The processing of some of these products requires large amounts of water and produces equally large amounts of wastewater. This water may be high in organic constituents and cyanide, which can pollute the ground water or the lakes, streams or rivers into which it is released. Other waste products resulting from cassava processing are often inadequately disposed of causing a foul smell and unattractive sight, and giving the cassava processing industry a reputation of polluting the environment (FAO and IFAD, 2001).

In the present study, the effect of cassava mill effluent on the fractionation of lead and cadmium in soil obtained from a refuse dump site was investigated.

MATERIALS AND METHODS

The major refuse dump site located about 150 m away from the capital guesthouse at the University of Benin, Benin City was used for the study. The refuse include metal scraps, used battery cells, papers, food cans, plastics, food materials and all sorts of assorted wastes. The waste occupies an area of 37 x 105 m with growing vegetation all around the refuse heaps.

Soils were collected at the base of the heaps using the soil auger. The sampling was done at every 20 m interval with a minimum of 5 cores collected at a spot. The core samples were bulked and the soil samples from the five spots covering the entire area were thoroughly mixed to make a composite sample and transferred into polyethylene bags. The soil depth sampled was 0-15cm,

Large particles were removed and the soil was spread on the rack at ambient temperature to dry, crushed in a porcelain mortar and sieved through a 2-mm (10 mesh) stainless sieve. Air-dried <2mm soils were treated with cassava mill effluents obtained from a cassava mill processing plant at Uselu market, Benin City. Selected physiochemical properties of the cassava mill effluents and the soils were determined.

The treatment rates of the cassava mill effluent on the refuse dump soils were as follows: All the samples were prepared in triplicates, and kept in the green house for 30 days. After 30 days, the soils were dried at ambient temperature, sieved again through a 2 mm (10 mesh) stainless sieve. The < 2 mm fraction soil was fractionated by selective sequential extraction and the extracts were analyzed for Pb and Cd.

Determination of soil physiochemical properties

Soil pH was measured in the laboratory with the aid of a Jenway Digital 330 pH meter following the procedure of Folsom et al. (1980). Organic matter (carbon) content was determined by the Walkley Black method (Nelson and Sommers, 1982), Total nitrogen was analyzed using a macro-kjeldahl method (USDA, 1972). Available phosphorus was determined by Bray and Kurtz method (Bray and Kurtz, 1945) while cation exchange capacity was estimated by summing exchangeable cations (cmo/kg) with the exchangeable acidity (Jackson, 1960). Particle size distribution was achieved according to the method of (Bouyoucos, 1962).

The pH of phosphorus, nitrogen, Ca, Mg; K, Na of the cassava mill effluents were determined by a modification of the appropriate method as applied to the soils.

Determination of Pb and Cd in the cassava mill effluent

Five milliliter of the thoroughly mixed CME was put in a digesting tube, following the addition of 15 ml concentrated 4 M HNO₃. The samples were digested for 8 hours. After cooling, the digest was filtered using Whatman no. 42 filter paper. The extract was analyzed for Pb and Cd using atomic absorption spectrophotometer (AAS) Bulk Scientific 210 GVP.

Fractionation of the soil

Each soil treatment was fractionated following a modification of the sequential extraction procedure to determine the metal binding forms (Tessier et al., 1979). By this procedure, variations of these metals in five binding phases (exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic and the residual form) were determined. The sequential extraction procedures are as follows:

Exchangeable: Soil (1g dry weight) was extracted with 20 ml of 1 M NH₄OAc (pH=7.0) in teflon centrifuge tubes for 30 minutes, with continuous agitation.

Bound to Carbonates: The residue from exchangeable fraction was extracted with 20 ml of 1 M NaOAc (pH 5.0 adjusted with HOAc) for 5 hrs with continuous agitation.

Bound to Fe-Mn oxide: The residue from the carbonate fraction was continuously extracted with 20 ml of 0.4 M NH₂OH.HCl in 25% acetic acid, for 6 hrs with continuous agitation at 96°C.

Bound to Organic: The residue from the Fe-Mn oxide fraction was extracted with 5 ml of 0.02 M HNO₃ and 10 ml of 30% H₂O₂ adjusted to pH 2 with concentrated HNO₃. The mixture was heated to 85°C for 2 hrs with occasional agitation. A second 6-ml aliquot of 30% H₂O₂ (pH 2 with concentrated HNO₃) was then added and the sample was heated again to 85°C for 3 hrs with intermittent agitation. After cooling, 15 ml of 3.2 M NH₄OAc in 20% (v/v) HNO₃ was added and the sample diluted to 20 ml and agitated continuously for 30mins.

Residual: The residue from the organic fraction was digested with a mixture of concentrated HNO₃ and HClO₄ for 6 hrs until the appearance of white fumes. The residue was dissolved in 12 M HCl and diluted to 25 ml.

Following each extraction or wash, mixtures were centrifuged at 1200 x g for 30 min. Prior to the start of the next extraction step, the residues were shaken with 8 ml distilled/deionized water for 30 mins, centrifuged, and the wash solutions discarded. The various filtrates were analyzed for Pb and Cd using atomic absorption spectrophotometer bulk scientific 210VAP.

RESULTS

Annexs 2 and 3 show the physicochemical properties of the refuse dump soil and cassava mill effluents respectively. The refuse dump soil was slightly acidic, with a pH of 6.2 while the cation exchange capacity was 31.37 cmol/kg. The soil was sandy loam with a mean sand fraction of 84.6%. The cation exchange site was dominated by calcium (24.0 cmol/kg). The high presence of Ca in the soil suggests that the refuse dumped at the site probably contained high amounts of calcium source materials. High mean phosphorus concentration (3160mg/kg) was obtained in the CME with a highly acidic medium (pH, 4.21). However, Pb and Cd were not detected in the effluents.

The distribution of Pb in the various fractions of the soil with the accompanying treatment with CME (Annex 4) showed that higher concentrations of Pb were detected in the carbonate fraction of the soil. There were also measurable amounts of Pb in the Fe-Mn ooxide and residual fractions respectively. The exchangeable fraction however had the lowest concentrations of Pb in all the fractions considered. It is important to note that treatment B (100ml CME) contributed to reduction in amount of Pb from the carbonate to the organic fraction, while there was an increased level of Pb in the residual fraction. This trend was affected by treatments A and C also in these fractions. Treatments D and E did not show any consistent pattern with respect to the distribution of Pb in these fractions. With the exception of the exchangeable fraction, there was a general reduction in amount of Pb detected in the soil due to the application of CME.

Similarly, the distribution of Cd in the different fractions of the soil corresponding to the treatment with CME is shown in Annex 5. Higher amounts of Cd were obtained in the carbonate fraction of the soil with treatments A and C respectively, implying that there was an initial high concentration of Cd in the soil carbonate fraction (treatment A). With the application of higher amounts of CME, increased Cd concentration was detected in the Fe-Mn Oxide fraction (treatments C and E). Equal levels of Cd were obtained in the organic fraction of the soil except with treatment E. The residual fraction had almost uniform distribution of Cd with the various treatments.

DISCUSSION

Mineral and organic soils can bind metals to different extent. Organic matter, Fe and Mn hydrous oxides, and clay content are significant soil properties influencing sorption reactions (Bolan and Duraisamy, 2003). Additionally, soil pH, cation exchange capacity (CEC) and redox potential can also regulate the mobility of metals in soils (Lombi and Gerzabek, 1998). Soil pH, for instance is very important for most heavy metals, since metal availability is relatively low when pH is around 6.5 to 7. In the present study, contributing low pH (4.2) by the CME would favor availability, mobility and redistribution of the metals Pb and Cd in the various fractions. On the contrary, the presence of carboxylic (-COOH) group (Grace, 1977) in the effluents favor complexation between CME and the metals. The overriding reaction would be determined by the amount (treatment) of CME applied to the refuse dump soil and other soil physicochemical properties. The observed pattern of decreasing concentration of Pb in the carbonate, Fe-Mn oxide and organic fractions as associated with increasing amounts of CME suggests that the presence of abundant complexing/chelating sites in the CME complexing with the Pb ions and perhaps adsorbed on the soil matrices may be responsible for this behavior. The relatively low amounts of Pb detected in the exchangeable fraction may be attributable to the low cation exchange capacity and low amount of clay in the soil. The high levels of Pb in the carbonate fraction can be attributed to the highly Ca dominated exchange site and fraction.

The non-detection of Cd in most of the treatments in the exchangeable fraction suggests that the exchange site may not have favored the availability of Cd. Furthermore, the presence of cations can affect metal adsorption in soils. For instance, Ca competes effectively with cationic heavy metals for adsorption and exchange sites, and this competition seemed to be greater for Zn and Cd than for Cu and Pb (KieKens, 1983; Pierangel et al., 2001; Pierangel et al., 2003). A higher level of Cd in the carbonate fraction implies that the carbonate fraction provided sites for binding of Cd at an optimum treatment of 200 ml of applied CME to the soil.

The rate of applied CME also had useful effect on the distribution of Cd in the Fe-Mn oxide fraction. The increased level of Cd in the organic fraction associated with treatment E may reveal the dominant effect of the highly reduced pH with high amount of CME thereby creating favorable conditions for the release of Cd.

CONCLUSION

The application of CME on the refuse dump soil showed depending on the applied rate that CME facilitated the reduction and redistribution of Pb in the soil, while it increased the mobility and availability of Cd in the soil. It was also seen that the major cationic composition of the exchange site in the soil contributed to the behavior and distribution patterns of the metals investigated. Depending on the dominant soil characteristics and type of heavy metal, CME can enhance its availability or reduce its mobility and occurrence in the soil.

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ANNEXES

Annex 1: Treatment rates of cassava mill effluents on refuse dump soil

Treatment	Amount of Soil (g)	Amount of CME (ml)
A	500	Nil
B	500	100
C	500	200
D	500	300
E	500	400

Annex 2: Mean selected physiochemical properties of the refuse dump soil.

pH	C %	N %	P (mg/kg)	cmol/kg										
				Na	K	Ca	Mg	H+	Al ³⁺	CEC	Sand	Silt	Clay	Texture
6.20	2.21	0.14	23.25	ND	0.37	24.0	5.20	1.17	ND	31.27	84.6	11.4	4.0	Sandy loam

Annex 3: Selected physicochemical properties of the cassava mill effluent (CME)

pH	mg/kg							
	N	P	Na	K	Ca	Mg	Pb	Cd
4.21	590.35	326.71	53.81	2396.12	250.81	430.0	ND	ND

ND = Not Detected.

Annex 4: Distribution of Pb (mg/kg) in the different fraction of the treated soil

Treatment	Exchangeable	Carbonate	Fe/Mn oxide	Organic	Residual
A	5.02	58.65	19.50	11.60	35.50
B	5.97	48.50	18.37	10.00	30.00
C	5.02	39.25	14.00	9.00	18.00
D	5.96	42.40	16.28	9.00	30.00
E	3.78	51.00	18.37	10.00	16.50

Annex 5: Distribution of Cd (mg/kg) in the different fractions of the treated soil

Treatment	Exchangeable	Carbonate	Fe/Mn oxide	Organic	Residual
A	0.00	7.90	0.20	0.20	0.70
B	0.00	3.50	0.30	0.20	0.80
C	0.00	8.20	5.50	0.20	0.70
D	0.00	3.70	0.30	0.20	0.60
E	0.00	4.00	5.30	3.30	0.70