

Application of Waste Cashew Nut Shell Ash Showed Significant Reduction in Mobility of Pb and Cd in Waste Battery Contaminated Soil.

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ABSTRACT

Increases in ore mining, metal smelting activities, and several other industrial practices in recent times have brought about contamination of soils at higher levels; these have prompted concerns on the consequent effects on the local and global ecosystem. Various remediation technologies have often been sought to meet the challenges. This study therefore seeks to assess the potential of cashew nut shell (CNS) ash for immobilizing Cd and Pb in battery contaminated soil. The ash samples used for the study were obtained from a waste cashew nut shell burning site, Olowopokun, Iseyin L.G.A of Oyo State, Nigeria. Some soil samples and sediments from a nearby stream at this site were taken. Soil samples were also taken from battery-contaminated dumpsites at Ile-Igbon, Lalupon, Oke-Omi, and Ikumapayi, in Lagelu L.G.A of Oyo State.

One gram each of ground soil samples, ash and sediment were analyzed for heavy metals contents. Ash generated from waste cashew nut shell from cashew nut processing company dumpsite were mixed with contaminated soil samples from the lead battery dumpsite at ratios 10:1.5 and 10:3.0. The amended and un-amended soil samples were subjected to TCLP in accordance with US Environmental Protection Agency (USEPA) Method 1311. Cd gave 97% efficiency in the reduction of its mobility in the amended soil while Pb gave 80% efficiency.

Increase in the quantity of CNS ash used for amendment from ratio 10:1 to 10:2 caused a rise in the pH of the soil, this translated to further reduction of the leached Pb and Cd from the soil. The assessment of the mobility of Pb and Cd in the soil as induced by the addition of CNS ash showed that there was reduction in the mobility of Pb and Cd from the contaminated soil samples as assessed by TCLP procedure. The use of the

CNS ash in stabilizing the contaminated soil served as an effective waste disposal method for waste CNS as well as source for remediation of contaminated soil. Waste CNS ash could be a great source for *in-situ* remediation of contaminated soil.

(Keywords: cadmium, lead, cashew nut shell ash, immobilization, remediation)

INTRODUCTION

Cashew (*Anacardium occidentale*) is one of Nigeria leading cash crops, being the world's 2nd largest producer of cashew. Nigeria produces 636,000 tons of cashew nuts yearly (FAO, 2008), most of which is mainly for the export market. The cashew nuts are exported either as whole shell or they are processed; and the cashew kernel exported. Cashew processing industries generate the cashew nut shell as a waste product; they utilize the waste cashew nut shell as a source of heat for their boilers, this result in waste ashes. The perennial nature of the crop means an abundance of waste cashew nut shell at the peak of the season, most processing industries resort to dumping of the excess waste cashew nut shell on open land and indiscriminate burning.

Managing waste ash generated from cashew nut processing is a major challenge; as land filling and open land dumping of the waste ashes are the main methods of waste management of the ash. Economically viable ways of using waste ash rather than having to dispose of it have to be investigated. There is already a vast body of information on utilization of fly ash (FA) in building/construction, production of aggregates and more recently for agriculture (Brian et al., 2003). Applying waste ash to agricultural land will be an opportunity to recover essential plant nutrients, reducing the dependence on

commercial fertilizers, help to reduce the acidity of the soil, as waste ash contain essential elements such as P, K, S, Ca, Mg, Na, etc., and micronutrients, which are essential for plant growth and has a high pH (Williams et al. 1976; Melbye et al.,1982. Theiss and Padget 1983; Jakobsen and Willet 1986, Lisk, 1988: Bierman and Rosen 1994).

Heavy metals such as Pb, As, Cu, Zn, Fe, and Mn have been recognized as important environmental pollutants, primarily in the area of public health (Kedziorek and Bourg, 1999). Intensive industrial activities have resulted in the accumulation of high concentrations of heavy metals and toxic elements in the soil environment causing serious socio-economic problems (Kaliampakos, 1998; Mavropoulos and Kaliampakos, 1999). These substances, when present in soils, are not biodegradable by natural process and remain in the ecosystem (Kedziorek and Bourg, 1999). Several remediation approaches may be applied to contaminated soil remediation, namely chemical treatment, soil flushing and washing, electrokinetic methods, bioremediation and phytoremediation techniques and thermal treatment (Mulligan et al., 2001). New technologies include the utilization of industrial by-products (like fly ash and slag) presenting high adsorption capacity with respect to metals (Moutsatsou et al., 2002). Ashes are used to stabilize or immobilize metals; during immobilization, inorganic contaminants can be converted to forms which are much less mobile, soluble and toxic (Conner, 1990).

The objective of the study is to find potential use for waste ash residue of cashew nut origin for its immobilizing capability of heavy metals in contaminated soil.

MATERIALS AND METHODS

Sample Collection

The ash samples used for the study were obtained from a waste cashew nut shell burning site, in Olowopokun, Iseyin L.G.A of Oyo State, Nigeria. Some soil samples at this site were taken at top soil level of 0-15cm and at a depth of 15-30cm; and a control soil sample was also collected. Sediments from a nearby stream were as well collected. The soil samples collected were made to reflect as much as possible the major parent materials in order to ensure that this soils

were representative samples of the prevailing soil condition.

Soil samples were also taken from battery-contaminated dumpsites at Ile-Igbon, Lalupon, Oke-Omi, and Ikumapayi, all in Lagelu L.G.A of Oyo State. One composite bulk sample each was prepared from randomly collected soil samples from the surface horizon (0-15cm), depth (15-30cm), control soil and sediments from the dumpsite. The same sampling method was used in collecting ash residues. The samples were collected in polyethylene bags and labeled accordingly.

Sample Treatment and Preparation

The samples were spread out to air-dry in a dust free environment over a period of two weeks. The air-dried soil samples were further treated by transferring them into a clean porcelain mortar and crushed gently with a pestle taking care that no stone, wood or dirt are grounded alongside. The grounded samples which were now fine particles were sieved through a 2.00mm mesh and the less than 2.00mm fraction retained. This fractions were thoroughly mixed to obtain a composite sample reduced by quartering to obtain a representative sample which were then stored in labeled Polyethylene bag for further laboratory analysis.

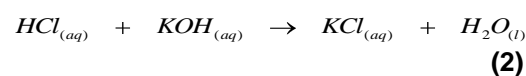
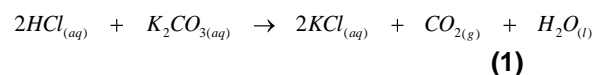
Determination of Cation Exchange Capacity (CEC), Batch Method.

The cation exchange capacity was determined using solution of 1.0M ammonium acetate (pH 7.0) extractable bases Ca, Mg, K, and Na. 5g each of the various soil samples top, depth, control and sediment were weighed accurately into 100ml polyethylene bottles and 30ml of ammonium acetate (1.0M pH 7.0) solution was added in each case. Each of these bottles was shaken thoroughly and left to stand for 2 hours. Thereafter they were centrifuged and each supernatant collected into 100ml standard flask. This extraction was repeated two more times each with 30ml NH₄OAC. The solutions were then pooled together in each case and made up to mark with NH₄OAC solution. The Ca²⁺, Mg²⁺, K⁺, and Na⁺ were determined using AAS, and emission mode, respectively.

Liming Effect (Acid Neutralizing Capacity) Analysis

A 5-g waste ash sample was weighed into a 500-ml volumetric flask, 100 ml of 1 mol l⁻¹ HCl added and left for 15 min; the flask was then closed with a rubber lid and shaken for 1 h; the mixture was diluted to 500 ml with distilled water and filtered; 80 ml of the filtrate was transferred into a 300-ml flask and diluted to 200 ml; then it was boiled for a couple of minutes. After cooling, eight drops of methyl red and methylene blue mixed indicator were added, and titrated with 0.1 mol l⁻¹ NaOH solution from purple to green (Page et al., 1979; Sander and Andren, 1997).

Equations for the reactions:



Let molar mass of K₂CO₃ = mmK₂CO₃

Let concentration of standardized HCl
= C_{HCl}

Let number of ml of HCl to be used in titration,
= V_{HCl}

Therefore moles of HCl used in titration:
n_{HCl} = C_{HCl} · V_{HCl}

Since stoichiometry of reaction is 1:2

Therefore number of moles of K₂CO₃ that was titrated:

$$nK_2CO_3 = \frac{1}{2} nHCl$$

Mass of unknown in sample analyzed: mK₂CO₃ = nK₂CO₃ · mmK₂CO₃

% of K₂CO₃ in the sample is given by:

$$\% K_2CO_3 = \frac{100 \times \text{Mass of } K_2CO_3}{\text{Mass of sample}} \quad (4)$$

Metal Analysis

1g each of ground soil samples, ash and sediment samples were weighed and placed in a beaker. 30ml of 1:1 HNO₃ (10ml water + 10ml concentrated HNO₃) were added and boiled gently on a hotplate until the volume is reduced to approximately 5ml while stirring. Further 10ml of 1:1 HNO₃ was added and the process repeated; it was cooled and the extract filtered through a Whatman No. 41 filter paper; the filter paper and beaker were washed with successive 0.25M HNO₃. The filtrate was transferred to a 50ml volumetric flask and diluted to the mark with deionized water. Sample was analyzed by atomic absorption spectroscopy (Radojevic and Bashkin 1999).

Contaminated Soil Amendment

Ash generated from waste cashew nut shell from cashew nut processing company dumpsite at Olowopokun in Iseyin Oyo State were mixed with contaminated soil samples from a lead battery dumpsite at ratios 10:1.5 (1g soil to 0.15g ash) and 10:3.0 (1g soil to 0.30g ash). The amended and un-amended soil samples were agglomerated by adding 10% by weight distilled water and mixing in rotating cylindrical containers. They were left to age for 60 hours prior to leaching (Ciccu et al., 2001).

Toxicity Characteristic Leaching Procedure (TCLP) Tests

All of the samples prepared and aged by the processes described above were subjected to TCLP in accordance with US Environmental Protection Agency (USEPA) Method 1311 (USEPA, 1992). An acetic acid (pH 3 or 5 depending on the soil pH) extract solution was used to leach Pb and Cd from the amended and un-amended soil samples which were shaken for 18 hours. The leachates were filtered through a 0.4µm pore size Whatmann filter paper. The filtered extracts were acidified with 0.2M HNO₃; then soluble Pb and Cd in the extract was measured using an atomic absorption spectrophotometer (AAS) (Buck Scientific Model 210).

Immobilization Efficiency (%)

The efficiency of the CNS ash to immobilize the heavy metals in the contaminated soil was calculated using the following relationship:

$$\% \text{Efficiency} = \frac{(\mu - \Lambda) \times 100}{\mu} \quad (5)$$

Where μ is the concentration of the leached metal before amendment with CNS ash, and Λ is the concentration of leached metal after amendment with CNS ash.

RESULTS AND DISCUSSION

Metal concentrations in the waste CNS ash compared with the levels in soil samples gotten from waste CNS ash dump site are illustrated in Figure 1. The values observed were ND-2.55mg/kg (Cd), 6.20-6.95mg/kg (Cr), 10.00-13.50mg/kg (Pb), 4.15-5.60mg/kg (Cu), 9060-9140mg/kg (Fe) and 8.80-13.10mg/kg (Zn); and in CNS ash, 1.50 ± 0.01 mg/kg (Cd), 53.10 ± 0.14 mg/kg (Cr), 142.00 ± 0.26 mg/kg (Pb), 80.40 ± 0.16 mg/kg (Cu), 7940.00 ± 5.00 mg/kg (Fe) and 726.00 ± 1.16 mg/kg (Zn). Macro element analysis showed lower concentrations. In soil, the concentrations were Ca, 1.47-1.50g/kg; Mg, 0.71-0.81g/kg; Na, 0.08-0.09g/kg; and K, 0.12-0.13g/kg.

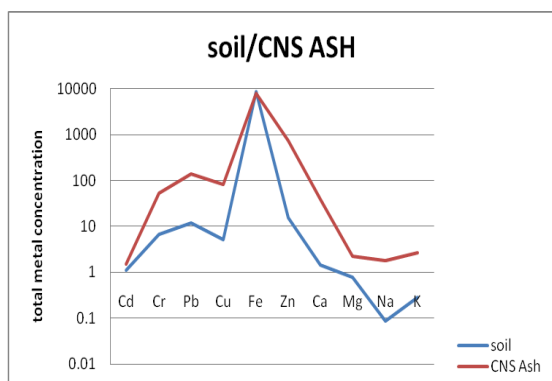


Figure 1: Metal Concentration in Soil from CNS Ash Dumpsite vs Metal Concentration in CNS Ash. Ca, Mg, Na, K are Expressed as gkg^{-1} while Cd, Pb, Cr, Cu, Fe, and Zn Concentrations are in mgkg^{-1} .

With the exception of Cd and Fe, CNS ash had higher values for all the metals than the soil samples collected from the waste ash dumpsite. There was no observable increase in soil concentrations of heavy metals as a result of the CNS ash. The levels of macro elements in the CNS ash were significantly higher than those of the soil sample. The concentration of K in the CNS ash was 9.5 times the level in soil; and the content of Ca, which is the main contributor to the liming effect, was higher in the CNS ash than in soil, 26.9 times; Mg and Na, 2.82 and 20.7 times higher, respectively.

High Fe concentration was obtained in both the soil and CNS ash samples; the values were slightly higher for both Top and Depth soil samples than the control sample, while the sediment sample had the least concentration of Fe (Table 1). Although a high Fe concentration was also detected in CNS ash, it was slightly higher in soil, as the soils contain high natural levels of Fe; high Fe concentration in the soil samples could have been added to from Fe in the ash. Heavy metals concentration in the soil samples were low for all metals analyzed. Cd in the top soil was below detection limit; while in the control, depth and sediment samples, there were observable levels. Pb in the top soil sample had higher concentration value than control, depth and sediment samples.

Soil pH for the entire soil sample analyzed was within neutral range; however the top soil had the highest pH value (7.36) while the sediment sample had the least (6.04); this could be attributed to the impact of the CNS ash on the soil.

The liming effect (acid neutralization capacity) expressed as CaO equivalent, is one of the most important indices used to evaluate the agricultural value of ash because waste ash tend to be used as a liming agent on acid soil. The CNS Ash has a neutralizing value of 24.1% expressed as Ca equivalents (equal to a value of 35.7% expressed as CaO equivalents).

The contaminated soils from the battery waste dump site contained high concentration of Pb with low concentration of Cd (Table 2). Leached solution from the contaminated soil sample showed high mobility of the Pb and Cd metals in the contaminated soil samples with two leached solution for Cd reading below detection limit.

Table 1: Main Characteristics of Top, Depth and Control Soil and Sediment Samples from CNS Ash Dumpsite.

Soil	Unit	Top soil	Control	Depth	Sediment
pH	-	7.36	7.01	6.90	6.04
Total carbon (TC)	%				
Organic carbon		1.17	0.83	1.54	1.45
Cation exchange capacity(CEC)	Cmolkg ⁻¹	3.45	2.70	2.87	2.88
Texture	%				
Sand	%	91.2	93.2	91.2	86.2
Silt	%	4.00	2.00	4.00	9.00
Clay	%	4.80	4.80	4.80	4.80
Elements (total concentration)	mgkg ⁻¹				
Cd	mgkg ⁻¹	ND	0.15	2.55	0.25
Cr	mgkg ⁻¹	6.95	8.10	6.20	6.85
Pb	mgkg ⁻¹	13.5	11.5	10	11.5
Cu	mgkg ⁻¹	5.6	5.05	4.15	5.7
Fe	mgkg ⁻¹	9140	8750	9060	7940
Zn	mgkg ⁻¹	13.1	14.5	8.80	24.1
Nutrients	gkg ⁻¹				
Ca	gkg ⁻¹	1.50	1.40	1.47	1.36
Mg	gkg ⁻¹	0.81	0.73	0.71	0.82
Na	gkg ⁻¹	0.09	0.08	0.08	0.09
K	gkg ⁻¹	0.13	0.12	0.12	0.60

Detection limit for Cd = 0.01

Table 2: pH, Metal Concentrations of Un-Amended and CNS Ash Amended Soil Leachate Samples.

Leachate	pH	Cd(mg/L)	Efficiency %	Pb(mg/L)	Efficiency %
Unamended soil (1)	5.00	0.59 ± 0.12		13.4 ± 0.40	
Unamended soil (2)	5.60	ND		9.40 ± 0.50	
Unamended soil (3)	6.20	ND		24.1 ± 0.15	
Unamended soil (4)	8.40	0.65 ± 0.15		14.1 ± 0.35	
Amended soil (1)	6.80	0.15 ± 0.02	75	3.10 ± 0.09	77
Amended soil (2)	7.40	ND		4.10 ± 0.10	56
Amended soil(3)	8.20	ND		8.60 ± 0.48	64
Amended soil (4)	10.2	0.021 ± 0.01	96	2.85 ± 0.02	80
Amended soil (1)	8.00	0.12 ± 0.02	80	2.79 ± 0.02	79
Amended soil (2)	8.90	ND		3.79 ± 0.02	60
Amended soil (3)	9.60	ND		6.90 ± 0.40	71
Amended soil (4)	11.2	0.02 ± 0.01	97	2.76 ± 0.02	80

ND (not detected): detection limit is 0.01 and 0.08 for Cd and Pb respectively. Triplicate analysis (\pm SD, n = 3). TCLP regulatory limit Cd = 1.0mg/L, Pb = 5.0mg/L.

Analysis of the leached solutions from the un-amended contaminated soil samples showed concentration values of 0.59 ± 0.12 mg/L, and 0.65 ± 0.15 mg/L respectively for Cd in un-

amended sample 1 (Ikumapayi) and un-amended sample 4 (Oke-Omi), while un-amended samples 2 (Ile-Igbon) and 3 (Lalupon) were undetected. Pb concentrations in the un-amended samples 1, 2,

3 and 4 were 13.4 ± 0.40 mg/L, 9.40 ± 0.50 mg/L, 24.1 ± 0.15 mg/L and 14.1 ± 0.35 mg/L respectively. Application of waste CNS ash to the soil showed a significant reduction in the mobility of Pb and Cd from the contaminated soil samples.

Cd through of a lower concentration in the un-amended soil, showed a greater efficiency in reduction of its mobility in the amended soil, where the highest efficiency was 97% and the lowest was 75%, respectively, than Pb, which had the highest efficiency of 80% and the lowest efficiency of 56% (Figure 2).

Increase in the quantity of CNS ash used for amendment from ratio 10:1 to 10:2 caused a rise in the pH of the soil; this translated further to reduction in mobility of the leached Pb and Cd from the soil, implying that higher pH as a result of the increase in CNS ash added to the soil sample increased the efficiency in immobilization of the metals. Increasing the quantity of CNS ash further was observed to lead to the solidification of the matrix.

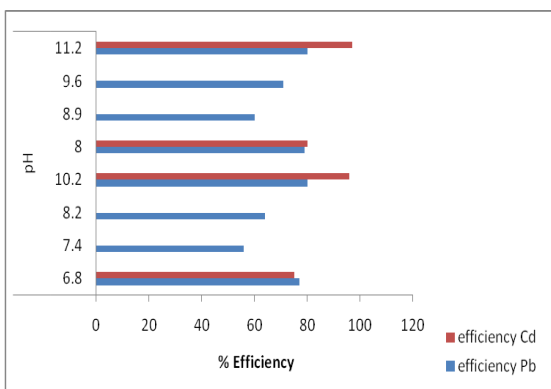


Figure 2: Percentage Efficiency Immobilization of Cd and Pb in Leachates of Soil Amended with CNS Ash at various pH Levels.

CONCLUSION/ RECOMMENDATIONS

It could be inferred from this investigation that CNS ash has the potential of immobilizing the heavy metals (Cadmium, and Lead) contained in severely contaminated soil; small addition of CNS ash can effectively reduce the Lead and Cadmium contents of the soil leachates. Hence CNS ash has good potential for In-Situ remediation of heavy metals contaminated soil. However this gives room for further investigation

of the effect of time, pH and other climatic conditions on the mobility of the metals in the soil.

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SUGGESTED CITATION

Ogundiran, M.B., J.O. Babayemi, and C.G. Nzeribe. 2011. "Application of Waste Cashew Nut Shell Ash Showed Significant Reduction in Mobility of Pb and Cd in Waste Battery Contaminated Soil". *Pacific Journal of Science and Technology.* 12(2):472-478.

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