

# ACCELERATED HEAVY METAL SORPTION FROM CONTAMINATED SOILS WITH ENHANCED PARTICLE SIZE COMPOSITE- EVIDENCED BY QUANTITY AND CONDUCTIVITY

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## ABSTRACT

Long resident time of accumulated heavy metals in soils is not good because of the resulting deleterious effects. It is therefore necessary to employ a quicker means of facilitating their removal as soon as their levels are ascertained. This investigation explored some properties of the saw dust (SD), egg shell powder (ESP) and high density polyethylene(HDPE) composites (sorbents) that could accelerate the sorption of metals from contaminated soils. The composites prepared by extrusion using a Jombo 300 Extruding Machine had the particle sizes of the saw dust and egg shells varied in the composites. The prepared composites were buried in the soil samples and at intervals of 3 days little portions of the soil samples were taken and analysed with Atomic Absorption Spectrophotometer(210 VGP Bulk Scientific ) and the results compared with the baseline values obtained prior to the burial of the composites. There was a corresponding increase in the concentration of the metals sorbed by the composites from the soil with particle size of the saw dust and egg shell powder. This increase was also evidenced by the decreasing conductivity of the soil samples with time as the metals were sorbed into the composites. There was no attenuation in the concentration of the metals even at the ninth day, suggesting a good efficiency span.

**Keywords:** Metals, composites, sorption, extruding machine, particle size, conductivity

## INTRODUCTION

Soil is a mixture of organic matter, minerals, gases, liquids, and organisms that together support life. Soil is a product of the influence of climate and relief (elevation, orientation, and slope of terrain), organisms, and its parent materials (original minerals) interacting over time. It continually undergoes development by way of numerous physical, chemical and biological processes, which include weathering with associated erosion. Given its complexity and strong internal connectedness, it is considered an ecosystem by soil ecologists (Ponge, 2015).

The Earth's body of soil is the pedosphere, which has four important functions: it is a medium for plant growth; it is a means of water storage, supply and purification; it is a modifier of Earth's atmosphere; it is a habitat for organisms; all of which, in turn, modify the soil. Soil consists of a solid phase of minerals and organic matter (the soil matrix), as well as a porous phase that holds gases (the soil atmosphere) and water (the soil solution), (Voroney and Heck, 2007).

Most soils have a dry bulk density (density of soil taking into account voids when dry) between 1.1 and 1.6 g/cm<sup>3</sup>, while the soil particle density is much higher, in the range of 2.6 to

2.7 g/cm<sup>3</sup> (Yu *et al.*, 2015). Little of the soil of planet Earth is older than the Pleistocene and none is older than the Cenozoic, although fossilized soils are preserved from as far back as the Archean (Retallack *et al.*, 2016).

Anthropogenic activities to a very large extent alters most of the veritable qualities of soil; heavy metal contamination of soil has become an issue of global environmental concern in recent years (Zhang *et al.*, 2013) due to waste emissions from industrial production, mining activities, wastewater, irrigation and inadequate management of pesticides and chemicals in agricultural production. All these activities have led to increasingly more contaminated soils worldwide which have caused and are still causing risk to human and/ or ecosystem health (Wuana and Okieimen, 2011).

The presence of heavy metals in soil reduces the pH of soil and surrounding water bodies by at least unit of 1 or 2 depending on the prevailing soil and environmental conditions (Dixit *et al.*, 1992a, Dixit *et al.*, 1992b); and thus reduces the abundance and biodiversity of soil microorganisms by its induced acidic soil condition which lowers soil fertility and crop yield by altering the carbon and nitrogen biogeochemical cycles (Dudka and Adriano, 1997). Therefore, the need for its removal or reduction in soil to tolerable levels.

Soil remediation technologies such as conventional soil reclamation practices, i.e. landfilling and excavation, are often very expensive and environmentally unfriendly, as compared to soil amendment based technologies, such as soil immobilization/solidification, which are cost effective and less environmentally disruptive (Kumpiene *et al.*, 2008, Mulligan *et al.*, 2001). However, the soil amendment based technologies are not fast, it takes weeks and months to effect a considerable removal of the heavy metals depending on the soil type. However, bio-waste composite with waste polyethylene heavy metal absorbents, are very much cheaper and eco- friendly. Besides, the constituents can be varied to explore improved performance, and they equally serve as a waste recycling route. This work therefore explores the influence of particles size of composite constituents on the acceleration of heavy metal sorption.

## MATERIALS AND METHODS

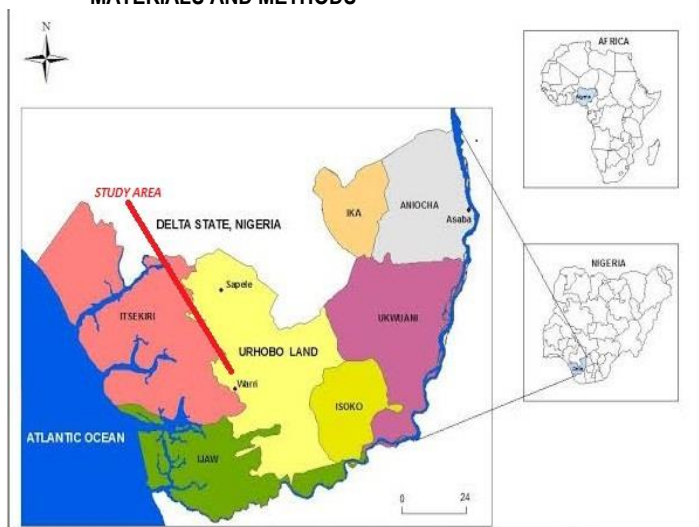


Fig 1: Map showing sampling location

### Sampling

The soil samples were collected very close to the waste dumpsite at the Federal University of Petroleum Resources, Effurun in Uvwie Local Government Area of Delta State, Nigeria within the coordinates 5°34'23"N and 5°50'38"E. The major activity around the sampling site is agricultural activity.

Waste polythene materials were collected from waste dumpsites within the premises of the University.

Egg shells were collected at a meat grilling (suya) spot at the entrance of the University and wood saw dust was collected from the timber market at Uti Street, about two kilometres from the University.

### Sample preparation

#### Soil

The soil samples were taken to the Department of Chemistry laboratory where the unwanted materials were removed from them.

#### Saw dust

The saw dust samples were hand-picked to remove unwanted particles, air dried and oven dried at 50°C to remove moisture. They were pulverized to reduce the particle size before sieving with sieves of different mesh sizes.

#### Polyethylene waste

The polyethylene wastes were washed with tap water, rinsed with distilled water and air dried to remove moisture before shredding.

#### Egg shell

The egg shells were washed with tap water several times and were rinsed with distilled water to remove contaminants, then air-dried and incubated in hot air oven at 40°C for 30 minutes (because protein component in egg shell can denature at high temperature greater than 40°C) (Singh and Gupta, 2016). Consequently, egg shells were ground to a powder in a grinder, and sieved to obtain between 0.15-1.18mm size particles (Singh and Gupta, 2016).

## METHODS

### Preparation of composite

Saw dust (SD), High density Polyethylene (HDPE) and Eggshell powder (ESP) composite were prepared in different proportions by weight where the HDPE served as the matrix to bind the SD and ESP.

#### Composite (1:1:1)

Equal weights of SD and ESP with particle sizes (0.150mm, 0.300mm, 0.425mm, 0.600mm and 1.18mm) and the same weight of HDPE were separately mixed together inside different bowls and introduced into the receptacle of a Jombo Extruder 300, at a temperature of 250°C to process the component particles and bind them together. The resulting molten products were collected in molds of the same dimensions; 29cm x 14cm x 1.5cm and allowed to cool before scaling them out.

#### Composite (2:1:1)

The same procedure as in composite (1:1:1) applied; the only difference is in the composition of the constituents; weight of the saw dust (SD) been twice the weights of polyethylene (HDPE) and egg shell powder (ESP).

### Metal sorption process

Before the commencement of the metal sorption process, a portion of the soil sample was collected and prepared for metal content determination using atomic absorption spectrophotometer (210 VGP Bulk Scientific) and conductivity test using a conductivity meter. These were to serve as a baseline reference for later determinations.

The composites (sorbents) were later buried in different portions of the soil samples which were properly shaken for intimate mixing. Little portions of each of the soil samples were collected at intervals of three days for atomic absorption spectrophotometric (AAS) analysis and conductivity test in order to determine the residual concentration of the metal in the soil and conductivity.

### Determination of metal concentration

1g of the soil sample was placed in a kjeldahl flask and 10mL of perchloric acid was added to it, and refluxed on a hot plate inside a fume cupboard for 2 hours. Thereafter, 50mL of distilled water was added to the digest and allowed to cool.

The digest was filtered and made up to 100ml mark of the volumetric flask with distilled water. It was transferred into a 120mL plastic container. The concentrations of the selected heavy metals were determined using Atomic Absorption Spectrometer (210 VGP Bulk Scientific).

### Conductivity

The conductivity meter (HANNA HI 98311) was calibrated with 0.1molar potassium chloride (KCl) solution.

1g of air dried soil sample was put into 100ml glass beaker and 10mL of distilled water was added and stirred. The mixture was allowed to stand for 30 minutes undisturbed. The electrode of the conductivity meter was carefully submerged into the beaker without touching the bottom of the beaker. The conductivity reading was taken after 30seconds. The electrode of the conductivity meter was rinsed within distilled water before each determination

**Quality control**

To ensure quality control, the samples were prepared and analyzed in duplicate in order to check the reproducibility of the method.

**RESULTS AND DISCUSSION**

**Table 1:** Baseline concentration of heavy metals (mg/kg)

Heavy metal	Pb	Cr	Cd	Fe	Ni	Zn
Conc(mg/kg)	17.50±0.3	19.75±0.37	5.75±0.01	1470±2.25	11.75±0.05	42.13±1.69

**Table2:** Concentration of heavy metals (mg/kg) absorbed by the composites (SD: HDPE: ESP) 1:1:1 after 3-9days

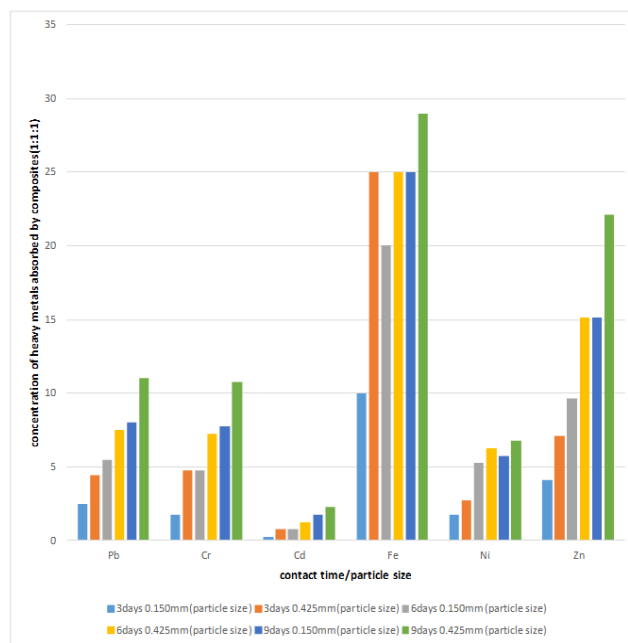
Time	Composite Particle size	Weight (kg)	Pb	Cr	Cd	Fe	Ni	Zn
3days	0.150mm	0.600	2.5±0.3	1.75±0.37	0.25±0.01	10.0±2.25	1.75±0.05	4.13±1.69
	0.425mm	0.600	4.4±0.3	4.75±0.37	0.75±0.01	25.0±2.25	2.75±0.05	7.13±1.69
6days	0.150mm	0.600	5.5±0.3	4.75±0.37	0.75±0.01	20.0±2.25	5.25±0.05	9.63±1.69
	0.425mm	0.600	7.5±0.3	7.25±0.37	1.25±0.01	25.0±2.25	6.25±0.05	15.13±1.69
9days	0.150mm	0.600	8.0±0.3	7.75±0.37	1.75±0.01	25.0±2.25	5.75±0.05	15.13±1.69
	0.425mm	0.600	11.0±0.3	10.75±0.37	2.25±0.01	29.0±2.25	6.75±0.05	22.13±1.69

**Table3:** Concentration of heavy metals (mg/kg) absorbed by the composites (SD: HDPE: ESP) 2:1:1 after 3-9days

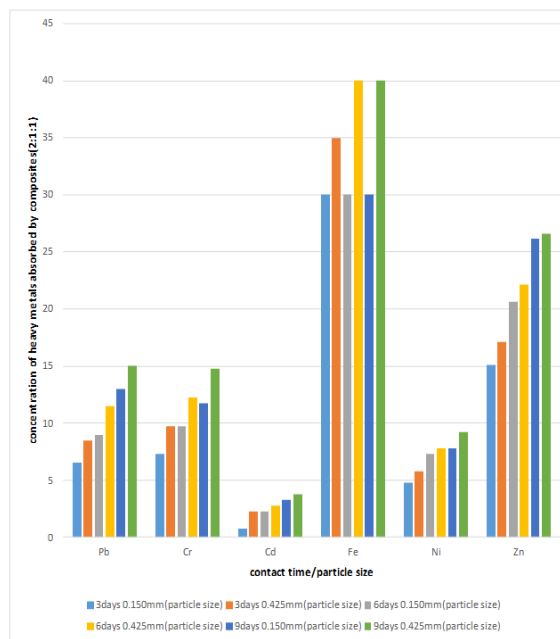
Time	Composites Particle size	Weight (kg)	Pb	Cr	Cd	Fe	Ni	Zn
3days	0.150mm	0.55	6.5±0.3	7.25±0.37	0.75±0.01	30.0±2.25	4.75±0.05	15.13±1.69
	0.425mm	0.65	8.5±0.3	9.75±0.37	2.25±0.01	35.0±2.25	5.75±0.05	17.13±1.69
6days	0.150mm	0.55	9.00±0.3	9.75±0.37	2.25±0.01	30.0±2.25	7.25±0.05	20.63±1.69
	0.425mm	0.65	11.5±0.3	12.25±0.37	2.75±0.01	40.0±2.25	7.75±0.05	22.13±1.69
9days	0.150mm	0.55	13.0±0.3	11.75±0.37	3.25±0.01	30.0±2.25	7.75±0.05	26.13±1.69
	0.425mm	0.65	15.0±0.3	14.75±0.37	3.75±0.01	40.0±2.25	9.25±0.05	26.63±1.69

**Table 4:** Conductivity of soil after 3-9days of immersion of composites

	(SD: HDPE: ESP) 1:1:1		(SD: HDPE: ESP) 2:1:1		
	Particle size	0.150mm	0.425mm	0.150mm	0.425mm
Initial		200	200	200	200
3days		150	137.9	142	115
6days		143	120.9	134	100.1
9days		122.1	103	111.1	96.02



**Fig.2:** Plot of concentration of heavy metals absorbed by composites (1:1:1) against contact time



**Fig.3:** Plot of concentration of heavy metals absorbed by composites (2:1:1) against contact time

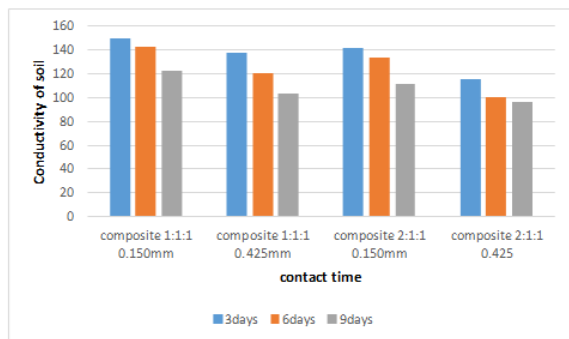


Fig.4: Plot of conductivity of soil against contact time

## Discussion

### Metal absorption capacity by composite ratio under 3 to 9 days

Composite ratio (2:1:1) sorbed higher metal concentration than the composite ratio (1:1:1) in the three time intervals of 3 days. For example, composite ratio (2:1:1) of 0.150mm particle size absorbed 30.00mg/kg of iron, 11.75mg/kg of chromium, 7.75mg/kg of Nickel, 13.00mg/kg of lead, 26.13mg/kg of Zinc, 3.25mg/kg of Cadmium after 9 days while composite ratio (1:1:1) of 0.150mm particles size absorbed 25.00mg/kg of iron, 7.75mg/kg of chromium, 7.75mg/kg of Nickel, 8.00mg/kg of lead, 15.13mg/kg of Zinc, 1.75mg/kg of Cadmium after 9 days.

This could be as a result of the relative increase in the amount of saw dust which provided increased number of pore spaces in the matrix thereby facilitating increased sorption of all the metals as shown on table 3 and figure 4.

In relation to the particle sizes of the saw dust and eggshell, there was a linear relationship between the concentration of sorbed metals and particle size. Increase in particle size resulted to increase in metal sorption despite the composite ratios as shown on tables 2 and 3. For example composite ratio (1:1:1) of 0.150mm particles size absorbed 25.00mg/kg of iron, 7.75mg/kg of chromium, 7.75mg/kg of Nickel, 8.00mg/kg of lead, 15.13mg/kg of Zinc, 1.75mg/kg of Cadmium after 9 days while composite ratio (1:1:1) of 0.425mm particles size absorbed 29.00mg/kg of iron, 10.75mg/kg of chromium, 6.75mg/kg of Nickel, 11.00mg/kg of lead, 22.13mg/kg of Zinc, 2.25mg/kg of Cadmium after 9 days. This is contrary to the results obtained by Kumarasywamy *et al.*, 2015, where the increase in particle size of egg shell powder decreased the adsorption of chromium in water. Though a different medium, the phenomenon exhibited here by the composites is contrary to one of the known laws of adsorption of Langmuir and Freundlich where reduction in particle sizes is said to result in increased number of pores and resultantly increased adsorption, though in liquid and gaseous media (Israel & Inam, 2014; Okafor *et al.*, 2013). This, perhaps was due to the matrix effect of the polyethylene medium which bound the particles of the saw dust and egg shell powder. The particles of the saw dust and egg shell powder created the pores on the polyethylene medium; so the bigger the particles's size the greater the pore space and increased sorption.

The contact time, which is the duration of burial of the composites in the soil samples equally influenced the concentration of the metals sorbed by the composites. At the intervals of three days, the concentrations of metals kept increasing. For example

composite ratio (1:1:1) of 0.150mm particles size absorbed 10.00mg/kg of iron, 1.75mg/kg of chromium, 1.75mg/kg of Nickel, 2.5mg/kg of lead, 4.13mg/kg of Zinc, 0.25mg/kg of Cadmium after 3 days. After 6 days the same composite ratio (1:1:1) of 0.150mm particles size absorbed 20.00mg/kg of iron, 4.75mg/kg of chromium, 5.25mg/kg of Nickel, 5.5mg/kg of lead, 9.63mg/kg of Zinc, 0.75mg/kg of Cadmium and after 9 days the same composite ratio (1:1:1) of 0.150mm particles size absorbed 25.00mg/kg of iron, 7.75mg/kg of chromium, 7.75mg/kg of Nickel, 8.00mg/kg of lead, 15.13mg/kg of Zinc, 1.75mg/kg of Cadmium. Interestingly, there was no attenuation in the concentration of the sorbed metals for the period of nine days. This showed that the composites have longer efficiency span for metal sorption as against crude oil sorption where attenuation could be reached in three days (Ibe & Pere in press). This could be as a result of the size of metal ions. The size of metal ions are comparatively smaller than the crude oil particles as crude oil is a conglomerate of many molecules. So, barring other flow factors like concentration and surface area, the metal ions will have greater mobility and hence faster sorption and above all will occupy less space than the crude oil particles.

### Conductivity

The conductivity of the residual metal ions in the soil taken at the same interval of three days corroborated the increased sorption of the metals with an inverse conductivity relationship as shown on table 4 and figure 4. As more metal ions leave the soil to the sorbent, there was a corresponding decrease in metal ion concentration in the soil, and since conductivity is a function of the concentration of ions, it is expected that there will be a decrease in conductivity of the soil with time.

### Conclusion

The composite ratios and the particles' size of the saw dust and the egg shell powder influenced the accelerated sorption of the metals by the composites (sorbents), though the influence of the particles' size was more prominent. The accelerated sorption of the metals by the sorbents was also evidenced by the corresponding decrease in the electric conductivity of the residual soil with time.

There was no attenuation in the concentration of sorbed metals with particles's size and contact time, which suggests an increased efficiency span.

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