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Remediation of Copper and Lead Contaminated Soil Using Inorganic Agents; Evaluation by Calcium Chloride and Ammonium Acetate

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Abstract- ***The soil sample collected had a pH of 6.50, a sandy percentage of 85.52, silt percentage of 5.28, clay percentage of 9.2, organic matter content of 3.25 and cation exchange capacity of 8.90 meg/100g. the soil was spiked with the salts to increase the metal concentration and incubated for two weeks. The contaminated soil was amended with natural clay and phosphate salt at different dosage levels and allowed to equilibrate for two weeks A 0.1m calcium Chloride and 1M ammonium acetate solution were used as extractants for bioavailable metal ions. The filtrate was analyzed with AAS. the result revealed that inorganic fixing agents such as natrual clay and phosphate salt are suitable for heavy metal immobilization. Since they reduced the concentrations of the metal ions available for plant uptake.***

Keywords: Remediation, Copper and Lead, Contaminated Soil, Inorganic Agents, Calcium Chloride, Ammonium Acetate

I. INTRODUCTION

Heavy metal contamination has become a common occurrence in developing countries as well as developed countries, due to increase industrialization and excess application of chemicals and fertilizers in agricultural activities. The situation is worse in developing countries such as Nigeria where environment regulatory agencies are non-existent or not adequately empowered to enforce environmental laws. Emphasis on the consequences of heavy metal contamination has been mainly on their detrimental health effects Jarup et al. (1998). Only Limited information exists on the effects of these contaminants on the soil productivity. Investigation and remediation of the effects of heavy metals on soil productivity is important because most often, the areas where heavy metal pollution occurs in developing countries are inhabited by the rural poor farmers who depend on the soil for their daily existence. Ehosien, (2004) Activities such as mining, manufacturing and use of synthetic products such as pesticide, Fertilizer, lead paints, batteries and industrial waste had resulted in many heavy metal contaminated sites. Over time heavy metal loading rate in soil has exceeded its natural removal rate in soil has by more than 20-fold. Contamination of soil by heavy metal is of major concern due to its high toxicity to human and total concentration exceeds 400mgkg-[1] USEPA, (1996. And remediation is required at this level.

In Nigeria for instance, a lot of heavy metal contamination has been reported on crop areas along highways. And those close to stone mining and quarry industries.

These areas of Nigeria are inhabited by resources poor farmers who depend on agriculture for their livelihood, the knowledge of the cost-effective remediation technique and the adverse effects of this heavy metal pollution in soil productivity will create the necessary awareness in government circles about the economic consequences of the heavy metal pollution. This would catalyze the relevant government agencies to make policies and regulations pertaining to environmental sustainability and conversation. Ano, (2007)

The importance of soil has lies in the interface between the earth atmosphere, lithosphere, and biosphere and hydrosphere; systems with which it continuously exchange matter and energy. This makes soil key to the development of surface biochemical cycles and gives it the ability to perform a series of essential functions within nature. Sponsito, (1989).

- Soil provides the nutrients, water and physical environment necessary for vegetative growth and

for the production of biomass, in general, playing a fundamental rote as food source for living organism.

- It is an essential component of the hydrological cycle acting as the distributing agent for surface water and distributing to ground water storage.

Despite efforts made by many countries to protect and preserve the social economic and environmental benefit of soil, heavy metal disposal is still a challenge word wide due to industrialization. Although soil itself can reduce mobility and bioavailability of heavy metals such as copper, yet immediate remediation measures in many heavily contaminated site is still required.

It is important therefore, to develop and effective and economic in situ technology to immobility heavy metal contaminants Chang et al: (2002)

Statement of Problem

Soil being the major reservoir for heavy metals released into the environment by the anthropogenic activities due to its ability to find various elements and these elements can exist in various forms and different forces keep them bond to soil particles. Unlike organic contaminants which easily oxidize to carbon dioxide by microbial action, most metals do not undergo chemical or biodegradations and their introduction into the soil changes their chemical form and bioavailability are however possible,

RISK associated with heavy metal contamination soils are:

Contamination of the food chain which is related to the ability of the metals to enter different components of the food chain, their availability to plants which are the essential component of the nature ecosystem and agro ecosystem, contamination of drinking underground water and unavailability of lands for agriculture activities.

Objectives of Study

1. The aim is to use these low-cost agent ‘i.e. natural clay and phosphate salt to immobilize copper.
2. To determine the physiochemical properties (Colour, PH, Texture, Organic matter and cation exchange capacity) of soil.
3. Determine soil total copper of soil sample before and after spiking the soil with the contaminants.
4. Access the factors relating to the effectiveness of the residues for the remediation of copper in contaminated soil sample.

Literature Review

Soil Formation and Properties

Soil is the collection of natural bodies on the earth surface in places modified or even make by man of earthly materials, containing living matter and supporting plants and other biomass. Soil includes the horizon near the surface that differs from the underlying rock materials as a result of interactions through time, or climate living organisms, parent materials and relief.

Nearly infinite variety of substance may be found in soil, these are categorized into four basic components. Mineral, Organic matter air and water the ideal oil. (Ideal soil for agricultural activities) It composed of 45% minerals, 25% water, 25% air and 25% organic matter in reality these percentages vary tremendously Grag et al (2006)

Soil Mineral

The minerals portion of the soil is divided into three particle size classes: Sand Silt and Clay. (These are collectively called the fine earth fraction of the soil). They area < 2mm in diameter, large soil particles are referred to as Rock sediment and have their own size classes.

Soil Contamination by Heavy Metals

Agricultural soils are contaminated by heavy metals that are mainly originated from mining activities, industrial automobile (Mechanic workshop) and traffic emission and agricultural practices such as application fertilizer, pesticides and sewage sludge to the soil.

Elevated heavy metals contamination in soil can lead to enhance crop take up and negatively affect crop growth and productivity. And that also pose danger on human and other being which feed on those crops Adam F.A. (2000).

There are many pollutants one of which is the heavy metal.

Heavy metals are defined as metals having density of greater than $5g/cm^3$ by Taraskevicus et al., and Radzevians A. (1999). They are classified into transition and atomic weight metals group III and IV of the periodic table.

Examples of heavy metals are copper, lead, zinc, cadmium, Arsenic, Mercury, cobalt, iron, Nickel, Chromium Adriano, (19866). Concentration of soil by heavy metal aries when metal is above a particular concentration which lead to the degradation of the soil qualities or elemental properties Marian E. (2000). Matals are natural components of the earth crust. They cannot be degraded or destroyed to a small extent; they enter our bodies through food, drinking water and air.

In most places where human activities are carried out especially on land a substantial amount of heavy metals which are toxic usually remain with dust particles.

Heavy metal contamination is problematic to children who through hand-to-mouth activities ingest as much as 90 milligram of dust or soil per day. Jarup (2008)

Source of Heavy Metals Contamination

Heavy metals are present in the environment and naturally constitute rock and sediments, as well as from anthropogenic sources. It is very difficult to distinguish between the natural metal enhancement and that of resulting from anthropogenic sources.

Anthropogenic emission of heavy metals into the environment may be direct into the air, water and soil. Olajire et al, (2003). Industrial discharges, Highway runoff and sewage effluent are responsible for most of the heavy metals in water.

Another source of heavy metal is the roads. Asphalt contains cobalt, nickel and zinc. These metals and other things that accumulated during dry spells will wash into nearby water bodies during any rain event.

Inorganic fertilizers which yield nitrates and nitride are widely distributed in the environment. These agricultural chemicals used in many ways to enhance a steady supplier at good quantities of food. Toxic elements like mercury and lead are contain s in these chemicals which tend to accumulate in soil, plants, even in aquatic organisms through the various mechanisms.

Therefore, human being maybe exposes to these metals through food chain, after the food might have been contaminated since all parts of environment interacts (Noller, 1989).

Further due to some modern agricultural particles, obnoxious pesticides, fungicide, biocide, bactecides etc. contaminate soil. Commercial and domestic urban wastes consisting old dried sewage sludge as well as garbage and rubbish materials such as plastics, metal cans, glasses, workshop sweeping (auto Mobil) paper, farm waste, soil conditional, soil fumigants, radioactive waste serve as source of soil pollutant. Combustion processes are the most important source of heavy metals, particularly, power generation, smelting, incineration and internal combustion engine (Nriagu,1989).

Occurrence, Properties and Health Effects of Heavy Metals

Lead (Pb)

Lead is a blush-white lustrous metal. It isvery soft, highly malleable, ductile, and a relatively poor conductor of electricity. It isvery resistant to corrosion but tarnishes upon exposure to air. Lead isotopes are the end products of each of the three series of naturally occurring radioactive element.

Native lead is rare in nature. Currently lead is usually found in ore with zinc, silver and copper and it is extracted together with these metals.

The main it led mineral is Galena (Pbs) and there are also deposits of cerussite and anglesite which are mined. Galena is mined in Australia, which produces 19% of the World's new lead. Followed by the USA, China, Peru and Canada. World production of new lead is 6 million tones a year, and workable reserves total are estimated 85million tones which is less than 15 years supply (Racek & Tretil, 2006).

Health Effects of Lead

Lead is one of four metals that have the most damaging effects on human health. It can enter the human body through uptake of food. (65%), water, (20%) and air (15%). Food such as fruits, vegetables, heats grains, seafood, soft drinks and wine may contain small amount of lead John M.K (1999).

Lead can enter (Drinking) water through corrosion of pipes. This is more likely to happen when the water is slightly acidic. That is why public water treatment systems are now required to carry out pH- adjustments in water that will serve drinking purposes.

Lead can cause several unwanted effects such as;

- A rise in blood pressure
- kidney Damage
- Miscarriages and subtle abortions
- Brain Damage
- Behavioural disruptions of children, such as aggression, impulsive behaviours and hyperactivity.

Environmental Effects of Land

Lead accumulates in the bodies of water organism and soil organisms.

These will experience health effects from lead poisoning. Health effects on shellfish can take place when only very small concentrations of lead are present.

Soil functions are disturbed by lead intervention especially near high ways and farmlands, where extreme concentrations may be present.

Soil organisms also suffer from lead poisoning.

Lead is a particularly dangerous chemical, as it can accumulate in individual organisms but also in entire food chain.

Lead can end up in water and soil through corrosion of leaded pipelines in water transporting system and through corrosion of leaded paints. It cannot be broken down: it can only be converted to other forms.

Cadmium

Cadmium (Cd) was discovered by Fredric Stronmeyer in 1817. It is a lustrous, silver-white, ductile, very malleable metal, it surface has a swish tinge and the metal is soft enough to be cut with a knife, but it tarnishes in air. It is soluble in acid but not in alkali

Cadmium is an element that occurs naturally in the earth crust. pure cadmium is soft. Cadmium is not usually present in the environment as pure metal but as a mineral combined with other elements such as oxygen (cadmium oxide). Chloride (cadmium chloride) cadmium is most present in nature as complex oxides, sulfides, and carbonates in zinc, lead and copper ones. These different forms of cadmium compounds are solids that dissolve in water to varying degrees. Cadmium may change forms, but the cadmium metal itself does not disappear from environment D. Amore et al., (2005).

Health Effects of Cadmium

Human uptake of cadmium takes place mainly through food. Stuffs that are rich in cadmium can greatly increase the cadmium concentration in human bodies. Examples are liver, mushrooms, shell fish, mussels, cocoa powder and dried sea weed.

Inhalation exposure to high level of cadmium in humans may result in effects on the lung, such as Brachial and Pulmonary Irritation.

- Long lasting impairment of lung function
- Chronic inhalation and Oral exposure of human to cadmium result in a buildup of cadmium in kidney that can cause kidney diseases such as proteinuria, decrease in glemenular filtration rate, kidney stone ASTOR (1999).

Environmental Effects Cadmium

Cadmium strongly absorbs to organic matter in soil when cadmium is present in soil it can be extremely dangerous as the Cadmium uptake through food will increase. This is a potential danger to animals that are dependent on plants for survival.

In aquatic ecosystem cadmium can accumulate in mussels, shrimps, lobsters and fish. The susceptibility to cadmium can vary between aquatic organisms' saltwater organisms are known to be more resistant to be cadmium poison than fresh water organisms.

Chromium (Cr)

Chromium is a lustrous, brittle, hard metal, its colour is silver-gray and it can be highly polished. It does not tarnished in air, when heated it burns and forms the green chromic oxide. Chromium is unstable in oxygen. It immediately produces thin oxide layer that is impermeable to oxygen and protects the metal below.

Chromium is mined as chromite (FeCr204) ore. Chromium ore are mined today in south Africa, Zimbabwe, Finland, India, Kazakhstan and Philippines. A total of 14 million tones of chromite ore is extracted. Serves are estimated to be of the order of 1 billion tones with unexploited deposit in Greenland, Canada and USA.

Health effects of Chromium

Chromium (Vi) is known to cause various health effects when it is a compound in leather product. It can cause allergic reactions, such as skin rash. It can also cause nose irritations and nosebleeds. Other health problems that are caused by Chromium (Vi) are:

- Upset stomachs and ulcer
- Respiratory problems
- Weakened immune systems
- kidney and liver damages
- Alteration of genetic material
- Lung cancer

Environmental Effects of chromium

There are several different kinds of chromium that differs in their effects upon organisms. Chromium enters the air, water and soil in the chromium (III) and chromium (Vi) form through natural processes and human activities.

The main human activities that increase the concentration of chromium (III) are still leather and textile manufacturing. The main human activities that increase Chromium (Vi) concentration are chemical, electro painting and other chromium (Vi) applications in industry. These applications will mainly increase concentrations of chromium in water. Through coal combustion. Chromium will also end up in air and through waste disposal. Chromium will end up in soils USEPA (1992).

Soil Amendment

Soil amendment is any material added to a soil to improve it physical properties such as water retention, permeability, water infiltration drainage, aeration and structure. The goal to provide better environment for roots to do this work, all amendment must be thoroughly mixed into the soil. If it is merely buried, its effectiveness is reduced and it will interfere with water and air movement and roots growth.

Inorganic Amendment

Inorganic amendments are used to improve substrate characteristics. These include quarry waste, pulverize refuse and pulverized fuel ashes. Inert materials including colliery spoils and steel slages are very often necessary to serve as an inulation layer to avoid migration to toxic element to the plants and ground water (Woney, 2003).

Blend of organic and Inorganic

The development of the additives used as metal fixation in soil is placing more emphasis on the reuse potential of the stabilized materials and the cost efficiency. Previous research had only concentrated on the reducing leachability efficiency of heavy metals after comparing with different additives.

Many amendments used in the stabilization of metals in MSW (Municipal Solid Waste) were introduced in contaminated soil remediation. The in-site remediation of contaminated soils by the fixation

method requires accurate cost assessment. And the ruse of stabilized material is of great consideration as well as the efficiency. In expensive, effective, readily available materials can be used in place of heavy metals in soils. A wide range of combined organic and inorganic amendments including low-cost sorbents such as xanthate sorbent had been studied.

Cement base and lime base additives were considered as the most effective in fixation. As for the fixation to metals in the soil, the lowest release of the previously immobilized toxic heavy metal components could be the foremost factor in choosing the additives for fixation.

Remediation of soil contamination

Remediation deals with the removal of pollution or contaminants from environment such as soil, groundwater, and sediments or surface water for the general protection of human health.

In last few years a considerable amount of research has been focused on trying to remediate heavy metal contaminated soils instead of destroying them. Soil destruction is generally out by taking soils to a properly isolated and controlled disposal site when it is felt that other remediation will be contained.

A wide range of heavy metal contaminated soil remediation technologies are currently available, some of which are routinely used and others which are still in their experimental stages designed to isolate or destroy the contaminating substances by altering their chemical structure, often times through chemical, thermal or biological processes.

The application of these technologies depends on the desired effectiveness of each method, on their economic viability and on the estimated time required to produce a significant result GWRTAC (1997).

Depending on how the soil remediating technique are applied, the term in-situ treatment is used when they act on the pollutants at the contamination site.

Ex-situ when the soil must first be equated for its subsequent treatment at the same location (On- Situ treatment) or at external facilities that required the contaminated soil to be moved (off site treatment).

In-situ requires les handling but in general are slower and more difficult to put into practice given the difficulty of exposing the de-contamination agents to the entire contaminated soil.

In contrast to many organic contaminants, the immobile and non-degradable natrue of heavy metals requires active remediation because natrual attenuation will do little to reduce its concentration.

Formation of insoluble heavy metal compounds immobilizes the metals and reduces their bioavailability Cotter et al., (1996).

There are several technologies available for the remediation of land contaminated with heavy metals. The selection of the most appropriate remediation technique depends on the site characteristics, concentration of pollutant, type of the pollutant of concern and the end use of the contaminated medium (Soil in this case). USEPA (2006).

The factors that may influence the applicability and selection of any of the available remediation techniques are:

a. Cost long term effectiveness/performances, commercial availability, General acceptance, applicability to high metal concentration, applicability to mixed case waste (Heavy metals and organic), toxicity reduction, mobility reduction and volume reeducation.

Single Extraction

This is the process of combining an organic solvent and water to form a bilayer (such as ether and water) in a vessel (for example a separating funnel) and then shaken to thoroughly mix the two solvents. The spefunnel is then allowed to stand which cause the mixture to separate into two layers which can be removed.

Materials and Method

Apparatus

- Flame Atomic absorption Spectrophotometer (Buck Scientific Model 200A)
- Multipurpose Flask Shaker (Model TT12F, Techmel, US)
- PH meter (Fisher Hydrus 300 model)
- Normal Laboratory glass ware (borosilicate)
- Polyethene vessels
- Electronic weighing; balance (Gallenkamp 80)

Chemicals and Reagents

- Acetic acid
- Hydroxylamine hydrochloride
- Ammonium Acetate
- Hydrogen Peroxide
- Nitric Acid
- Ethylenediaminetetraacetic acid EDTA
- Sodium hexametaphosphate (5%)
- Potassium dichromate

Study Area

Makurdi is a rapidly growing city located at the coordinates 7.44^0N, 8.33^0E in the lower Benue river basin, a major agriculture zone in central Nigeria. the city itself bisected by Benue River into the North-bank and south-bank areas. The soil are derived from the pre-Cambrian basement complex rocks and quaternary alluvial deposits of the river Benue as parent material. The range of annual rainfall is 1200-1650mm and is distributed between March/April and November/December. Followed by a marked yr. season (of up to four months). The ranges of daily maximum and minimum temperatures during the rainy season are 30-34^{0}C and 22-24^{0}C, respectively and 33-37^{0}C and 18-24^{0}C, respectively in the dry season. Daily global radiation and mean hours of insulation are respectively 314-433 cal.cm^{2}day^{-1} and 4.00-7.74 h. There is no central sewage collection and treatment system within the municipality and so untreated sewage sludge from filled residential septic tanks are eventually mechanically emptied and transported to the layout for disposal on open land where no regulations are practiced. Similarly, other solid and liquid wastes generated by industries within the layout and other parts of urban Makurdi are indiscriminately disposed of at the layout. Risks from heavy metal contamination of these soils are possible since urban agriculture is simultaneously practiced at the layout.

Procedure for the Extraction of Copper and Lead using Ammonium Acetate

1m of ammonium acetate using and 2g of soil sample measured with 25 mil of solution shaken thoroughly and allow to stand for 90 minutes and extracted using what-man filter paper.

Procedure for the extraction of Copper and Lead using $cacl_2$

0.1m of cal_2 used and 2.5g of soil sample measured with 10 mil of solution, shaken thoroughly and allow to stand for 120 minutes and extracted with what-man filter paper.

Soil Amendments with Metal fixing agents

Different fixing agents- natural cly, phosphate salt, $Ca_3 (PO4)_2$ (Previously characterized in terms of some physiochemical attributes) were used to compare and evaluated their effectiveness at fixing Cu an Pb in contaminated soil. Different portions of a fixed mass of soil (50g soil moistened with water) were separately put in polyethylene bottles and treated with 10%, 20% 30%, 40% and 50% of the triplicate and incubated for 2 weeks at room temperature.

Quality control and Statistical Treatment of Data

The accuracy and reliability of the results was ensured by the use of analytical grade chemicals to prepare standard solution and regents. All glassware and plastics were acid- washed. Standard solutions were used to calibrate the AAS

Results

Physiochemical Characteristics of Parent Soil and Fixing Agents used for the Study

Property	Parent soil	Natrual Clay	$Ca_3(PO4)^2$
Soil pH	6.5	6.72	8.0

Sand (%)	85.52	30	-
Silt (%)	5,28	21.5	-
Clay(%)	9.2	47.5	
CEC(meq/100g)	8.90	7.33	-
Organic Matter Content	3.25	4.33	-

(CH_3COONH_4) Extracted * Cu and Pb Concentrations (mg kg^{-1}) in soil amended with different doses of fixing Agents

S/N	$CH_3COONH4$ Doose (%)	CU	Pb	Binary Metal Contamination	
				CU	Pb
1.	10	0.068	0.083	0.060	0.081
2.	20	0.062	0.073	0.048	0.067
3.	30	0.014	0.046	0.030	0.050
4.	40	0.012	0.014	0.022	0.034
5.	50	0.011	0.002	0.008	0.030

S/N	Cacl2(mg/kg Dos (%)	(Cu)	Pb	Binary metal Contamination	
				CU	Pb
	10	0.051	0.0048	0.0039	0.0042
	20	0.042	0.0041	0.0032	0.0036
	30	0.040	0.0034	0.0027	0.0031
	40	0.028	0.0033	0.0021	0.0029
	50	0.021	0.0028	0.0019	0.0022

Coal2 Extracted * Cu and Pb concentrations (mg kg-) in soil amended with different doses of fixing agents

The study revealed the suitability of inorganic amendments such as natural clay and phosphate salt for heavy metal immobilization in contaminated soil. Also, it showed the extend of heavy metal immobility by the inorganic ammendments depends on the amount of the residue and the concentration of the heavey metals.

Based on the result obtained inorganic amendment such as natural clay and phosphate salt are recommended as suitable and effect for immobilization of heavy metal in contaminated soil.

Conclusion

Soil samples were taken from the premises of University of Agricultrue Makurdi: at the back of block B and was analyzed for its physiochemical properties. The soil samples were spiked with Pb ($N0_3$) and ($CuN0_3$) in order to increase the concentration of the contaminants to appreciable amount. the spiked soil samples were incubated for two weeks with daily mixing. The contaminated soil was amended with inorganic amendment such as natural clay and phosphate salt and was incubated for another two weeks with daily turning, in order to investigate for (i) the effect of different level of amendments on metal immobilization (ii) the effect of increasing level of the metal in soil in their immobilization. 2.5g portion of the amended soil was extracted with Cacl2 and 2g of portion of the amended soil was extracted with CH_3COONH_4 and the supernatant was analyzed for available metal using AAS.

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