CHAPTER 4

Assessment and Remediation of Heavy Metals Contaminated Soils

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BACKGROUND INFORMATION

Heavy metals contamination is a global issue that has generated a lot of concern in all parts of the world and which requires both local and universal attention to stem the growing threat it poses to survival on earth. The world has witnessed dramatic advancements in science and technology in the past two centuries. These technological breakthroughs have been deployed variously to tackle and solve many problems of man, which, in effect, has led to overall improvements in the general standards of living. However, with every new invention or breakthrough comes new challenges and responsibilities. Heavy metals reach and contaminate the environment from myriad of human activities, the common ones being industrial activities, agricultural practices, waste and waste disposal sites, sewage sludge and automobiles. As the aftermath of many scientific innovations the world has witnessed, is the growing challenge of coping with the proper disposal of the used products and wastes of the new discoveries. Majority of the wastes, particularly metallurgical and electrocic (E-waste) wastes have been reported to contain heavy metals among other things (Piatak *et al.*, 2015; Song and Li, 2015). Some of these heavy metals may be minute in their presence but are damaging to human health, toxic to plants and aggravate alteration in the ecosystem of aquatic and terrestrial animals.

Although water and air contamination is also inimical to human health and existence, soil contamination by heavy metals has attracted considerable concern worldwide. The reasons are because heavy metals in soil are non-biodegradable, can metabolise into bioavailable forms and persist in the soil over a long period of time more than other compartments of the earth. Lead, cadmium and zinc have been reported as few of the persistent heavy metals whose soil retention times have been estimated to be from 150 to 5000 years (Kumar *et al*., 1995), 13 to 1100 years and 70 to 510 years (Kabata-Pendias and Pendias, 2001), respectively.

HEAVY METALS IN THE ENVIRONMENT

Heavy metals are chemical elements with a specific gravity of about 5.0g/dm^3 or greater (Bolan and Duraisamy, 2003). Examples of heavy metals include arsenic, cadmium, chromium, copper, lead, mercury, nickel, iron, selenium and zinc. Some well-known toxic heavy metals with a specific gravity that is greater than 5.0 g/dm^3 are arsenic, 5.7 g/dm^3 ; cadmium, 8.65 g/dm^3 ; iron, 7.9 g/dm^3 ; lead, 11.34 g/dm^3 ; and mercury, 13.5 g/dm^3.

Sources of Heavy Metals Contamination in Soils

Metals enter the environment from a variety of natural and anthropogenic sources. Most soils normally contain low background levels of heavy metals. However soil contamination with heavy metals may occur as a result of waste from agricultural, manufacturing, pharmaceutical, industrial processes, or domestic activities. Various sources may finally reach the surface soil and their fate depends on soil chemical and physical properties and especially on their speciation.

Natural occurrence of heavy metals in soils

Heavy metals can be inherited from lithogenic activities i.e from the mother material such as weathering of rock, erosion, volcanoes and forest fires. The concentration of metals in uncontaminated soils has been said to be primarily related to the geology of the parent material from which the soil was formed (McLean and Bledsoe, 1992). Natural processes rarely result in elevated concentrations in the environment. Lead is naturally occurring and it is obtained chiefly from galena (PbS) by a roasting process. Anglesite, lead sulphate ($PbSO_4$), cerussite, lead carbonate ($PbCO_3$), and minim (Pb_3O_4) are other common lead minerals. It occurs in all soils with its terrestrial abundance in soils ranging from 1 to 200 ppm with a mean of 15 ppm (Zimdahl and Skogerboe, 1977). Cadmium is a relatively rare element and most often it occurs in small quantities associated with zinc ores, such as sphalerite (ZnS). Greenockite (CdS) is the only mineral of any consequence bearing cadmium. Cadmium is widely distributed in the earth's crust with concentrations ranging from 0.1-1.0 mg/kg and an average concentration of about 0.1 mg/kg (WHO, 1992). Chromium is a naturally occurring element found in rocks, animals, plants, soil, and in volcanic dust and gases. The major ore of chromium is ferrochromite ($FeOCr_2O_3$) (Zayed and Terry, 2003). Chromium is found in all soils as Cr (III). In most soils, chromium (III) occurs in low concentrations (2-60 mg/kg). On the other hand, occurrence of Cr (VI) is mainly the result of human activities. Chromium (VI) occurs naturally in the rare mineral crocoite ($PbCrO_4$). The natural occurrences of Ni are mostly mixed ore sulphides with iron or copper, but it is also present in elevated concentrations in pyrite (FeS_2). Nickel is found in all soils at varying concentrations. Farm soils contain between 3 and 1000 mg/kg (WHO, 1991). Zinc is one of the most common elements in the earth's crust. The most important zinc minerals in the world are sphalerite (ZnS), smithsonite ($ZnCO_3$), and hemimorphite ($Zn_4Si_2O_7(OH_2).\ H_2O$). The natural background zinc concentration in soil is 10-300 mg/kg (WHO, 2001).

Anthropogenic sources of heavy metals in soils

Anthropogenic metals are those deposited into soils as a result of direct or indirect human activities. There has been assumption that behavior of trace elements in soils and in consequence their bioavailability differs as their origin (Kabata-Pendas and Pendas, 2001). Anthropogenic contamination of soils has received international attention and many works have been documented on this issue (Ogundiran and Osibanjo, 2009b; Bi *et al*., 2006; Boularbah *et al*., 2006; Bunzl *et al*., 1999; Cartwright *et al*., 1976). It is of great concern both in the developing and developed countries of the world. This attention is necessary to safe guard the environment and the living organisms. The most commonly determined heavy metals at contaminated sites include lead, cadmium, chromium, nickel and zinc. The specific type of heavy metal contamination found at a contaminated site is directly related to the operation at the site. Automobile, agricultural activities, active and old mining, metal processing industry, among others have been identified as the major sources of high levels of heavy metals in soils.

Studies have identified emissions from automobiles as sources of heavy metals, particularly Pb, in roadside soils (Sisman *et al*., 2004; Onianwa, 2001). Agriculture activities tailored towards improving soil fertility can result in soil contamination by heavy metals. Heavy metal inputs from agricultural activities include those from use of biosolid, commercial fertilizers, liming materials, agrochemicals, sewage sludges, irrigation waters and other wastes used as soil amendments (Sposito *et al*., 1982; Shumah, 1998). Elevated concentrations of heavy metals are generally found in soils around abandoned and active mines due to the discharge and dispersion of the mines' waste materials by runoff or wind. (Piatak *et al*., 2015; Ogundiran and Osibanjo, 2012; Boularbah *et al*., 2006; Sanghoon, 2006; Bi *et al*., 2006; Myung, 2001; Onianwa and Fakayode, 2000; Bunzl *et al*., 1999; Cartwright *et al*., 1976).

Chemistry of heavy metals in soils

The behaviour of heavy metals in the environment in terms of mobility and availability is controlled by the chemical forms of the heavy metals in the soils (Taylor *et al*., 1995). Heavy metals reaching the soil undergo several reactions with different soil constituents, which in effect affect their solubility, mobility and availability to plants (Scokart *et al.*, 1983). The chemistry of heavy metals in soil can be be influenced by several soil processes. These processes are classified as cation exchange, adsorption, precipitation complexation with organic matter and redox reaction, although, clear distinctions cannot always be made between the processes (Rieuwerts *et al.*, 1998).

Factors affecting the content and distribution of heavy metals in soils

The bioavailability, mobility and toxicity of heavy metals in soils are generally influenced by major factors, which include pH, organic matter, soil texture and Fe-Mn oxides (Cieslinki *et al.* 1996). Concentrations of soluble and plant available metals are generally believed to be controlled by the pH of the soil (Rieuwerts *et al.*, 1998). Metal solubility tends to increase at lower pH and decrease at higher pH values (Chuan *et al.*, 1996). Soil pH values below 5.0 to 5.5 may indicate solubility of metals which if high enough may be biologically toxic (Kotoky *et al.*, 2003). Retention of metals by organic matter occurs by complexation and adsorption. The formation of soluble complexes with organic matter has been found to result in the solubilisation of Cd, Pb and Zn as cited by Walter *et al* (2003).

PATHWAYS OF EXPOSURE AND TOXIC EFFECTS OF HEAVY METALS ON THE ECOSYSTEM

Human and animals may be exposed to heavy metals through ingestion of metal-contaminated food and water, inhalation of metal-containing particles of soil or dust in air and dermal absorption.

The effects of heavy metals can be acute or chronic. Acute toxicity is usually from a sudden or unexpected exposure to a high level of the heavy metal. Chronic toxicity results from repeated or continuous exposure to low levels of the heavy metals through ingestion, inhalation or dermal contact, leading to an accumulation of the toxic substance in the body. Chronic exposure may result from contaminated food, air, water, or dust.

In the environment, heavy metals are known to be toxic to microorganisms, plants, animals and man in highly contaminated soils. They reduced the population of microorganisms, especially fungi, caused impaired development and reproduction in nematode and caterpillar (WHO, 1989), and inhibited stomata opening, photosynthesis and transpiration in plant. They are also responsible for chlorosis (yellowing), stunted root growth and brown interveinal necrosis in plant (Rooney *et al.*, 2007; Bazzaz *et al.*, 1974). For mammals and birds, kidney damage by Cd was reported. Elevated levels of Pb, Cd and Zn in the blood of birds and cattle grazing near a Zn smelter have been reported and red blood cell delta- amino levulinic acid dehydratase (ALAD), a sensitive indicator of metal exposure was reported in birds and mammals (Nelson *et al.*, 1985). Exposure of humans to heavy metals in the environment can cause serious acute or chronic health effects. In humans, exposure to lead has been associated with cardiovascular, hematological, musculoskeletal effects, effects on teeth in children, renal effects, alterations in serum hormone levels, cataracts, altered vitamin D metabolism, neurological effects, reproductive effects, altered children's growth, decreased erythropoietin in children and possibly increased risk of lung cancer and stomach cancer in lead workers (WHO, 2006; Kakkar and Jaffery, 2005). Chronic exposure to high levels of cadmium can cause kidney and liver damage in man. Cadmium is a known human carcinogen (Kakkar and Jaffery, 2005). Long-term exposure to hexavalent Cr has been associated with high incidence of respiratory cancers (Kakkar and Jaffery, 2005).

REMEDIATION TECHNIQUES FOR HEAVY METAL CONTAMINATED SOILS

Remediation techniques have been designed to reduce soil heavy metal bioavailability. Many methods have been used to decontaminate metals-contaminated soils and make the soils relatively safe for the environment and humans. The commonly employed methods include containment, biological treatments, solidification/stabilisation and immobilization.

Containment

In containment technique, contaminated site is separated physically so as to prevent the transport of heavy metals from the contaminated site by curtailing them within a designated area. The technology is mostly applied when other treatment options are not physically or economically feasible for a site. Physical separation of contaminated soil are done through capping, soil washing or by ex situ techniques i.e. excavation and dumping of soil to a designated landfill site.

Biological Method

Biological treatment of heavy metal-contaminated soil makes use of natural biological processes that allow microorganisms (bioremediation or microbial remediation) and certain plant species (phytoremediation) to aid in the remediation of metal-contaminated soils. Biological treatment method is limited to shallow depths of contamination (Mulligan *et al.*, 2001).

Microbially mediated remediation method can occur through a variety of mechanisms, including adsorption, redox reactions and methylation. Bacteria, yeast and fungi isolated from contaminated sites possesses excellent capability of metal scavenging (Malik, 2004). In phytoremediation, the pollutant is gradually removed from the soil by plant uptake and harvesting. This remediation method has attracted attention in the recent years due to the low cost of execution when compared to other remediation techniques and environmental friendliness. Phytoremediation technologies that have been applied for remediation of metals-contaminated soils include phytostabilisation and phytoextraction. Phytostabilisation technique involves the use of plants to restrict the movement of heavy metals out of the contaminated soil. Plant species that are used to stabilise heavy metals in contminated soil have high tolerance of metals in surrounding soils but low accumulation of metals in the plant. Phytoextraction is based on the use of natural hyperaccumulator plants with exceptional metal-accumulating capacity to reduce the levels of bioavailable metal in heavy metal contaminated soils. These plants have several beneficial characteristics such as the ability to accumulate metals in their shoots and an exceptionally high tolerance to heavy metals (Kidd and Monterroso, 2005). Hyperaccumulators have been defined as plant species which contain more than 0.1% (1,000 mg/kg) of copper, lead, nickel chromium or cobalt, cadmium >100 mg/kg in their dried tissues. In the case of zinc and Mn, a threshold of 1% (10,000 mg/kg) is proposed (Boularbah *et al.*, 2006). In addition, a hyperaccumulator is regarded as plant which the concentrations of heavy metal in its above ground part are 10-500 times more than that in usual plant.

Solidification/Stabilisation Technique and Immobilisation Techniques

Metals-contaminated sites have been treated with solidification/ stabilisation and immobilisation methods using inorganic and organic amendments. These technologies are designed to reduce the mobility of heavy metals by changing the physical or leaching characteristics of the contaminated soils. Solidification/stabilisation involves the formation of a solidified matrix that physically binds the contaminated soil to convert the heavy metals in the soil to a less mobile form (Mulligan *et al.*, 2001). Inorganic binders, such as Portland cement, fly ash, or blast furnace slag, and organic binders such as bitumen are used to form a crystalline, glassy or polymeric framework around the heavy metal-contaminated waste or soil (Ogundiran *et al.*, 2013; Dermatas and Meng, 2003; Yilmaz *et al.*, 2003).

Immobilisation is a site remediation technique in which chemicals are applied to the contaminated soil in-situ to alter soil heavy metal chemistry, through metal adsorption or complexation or precipitation, making the contaminant less soluble, less mobile and less bioavailable (McGoween *et al.*, 2001). In-place immobilisation does not affect the total contaminant concentration, but reduces the risk of harm to a target organism such as humans, animals and plants. Immobilsation technology has been associated with cost-effectiveness in remediating heavy metal contaminated sites. A range of inorganic and organic chemicals have been applied to heavy metal contaminated soils to immobilise heavy metals in soil. Some of these chemicals include phosphate compounds, lime materials, dolomite, iron hydroxides, manganese oxides or zeolite and and organic amendments.

Phosphate Chemicals

Out of all the chemical methods, phosphate application has been widely studied to remediate heavy metals contaminated soils, particularly, lead-contaminated soils (Ogundiran and Osibanjo, 2009a; McGoween *et al*., 2001; Hettiarachchi *et al*., 2000). Phosphate compounds have received wide application as chemical amendments for the following reasons; low cost, ease of implementation of the treatment, best overall results, in-situ application and production of little or no disturbance on the environment. It is fast in action and the lead pyromorphites formed is highly insoluble and stable. The major phosphate chemicals that have been used are mineral apatites {Fluorapatite [$Ca_{10}(PO_4)_6F_2$], hydroxyapatite [$Ca_5(PO_4)_3OH$]}, phosphate rock, calcium hydrogen phosphate ($CaHPO_4$), potassium dihydrogen phosphate (KH_2PO_4), mono-($NH_4H_2PO_4$) and diammonium ($(NH_4)_2HPO_4$) hydrogen phosphate and phosphoric acid. Each of these chemicals has advantages and disadvantages attached. However, all of them give rise to the expected results if properly applied. The reaction between Pb and phosphate compounds have been documented to result in any of the following pyromorphite compounds, hydroxypyromorphite [$Pb_5(PO_4)_3OH$], chloropyromorphite [$Pb_5(PO_4)_3Cl$], or fluoropyromorphite[$Pb_5(PO_4)_3F$] depending on the concentrations of Cl^- , F^- and OH^- ions in soil (Essington *et al*., 2004). Using hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$ as an example, Ca will be substituted with Pb resulting in highly insoluble Pb-phosphate minerals as shown in the equations below:

$$Ca_{10}(PO_4)_6(OH)_2\ (s) + 14H^+\ (aq) \xrightarrow{\text{Dissolution}} 10\,Ca^{2+}\ (aq) + 6H_2PO_4^-\ (aq) + 2H_2O\ (l)$$

$$10Pb^{2+}\ (aq) + 6H_2PO_4^-\ (aq) + 2H_2O\ (l) \overset{\text{Precipitation}}{\leftrightarrows} Pb_{10}(PO_4)_6(OH)_2\ (s) + 14H^+\ (aq)$$

Liming Chemicals

Liming chemicals such as Calcite ($CaCO_3$), burnt lime (CaO), slaked lime [$Ca(OH)_2$], dolomite [$CaMg(CO_3)_2$] and slag ($CaSiO_3$) have also been used to immobilise metals in contaminated soils (Bolan and Duraisamy, 2003; Brallier *et al.*, 1996). This was done to increase the pH of the contaminated soil thereby reducing the availability of the the toxic metals.

Iron Hydroxides, Manganese Oxides or Zeolite

Iron hydroxides, manganese oxides or zeolite have also been employed to increase the adsorption sites of heavy metals in soils. Some reports have indicated that the application of hydrous oxides of iron (FeOOH), manganese or zeolite (that is crystalline alumino silicate minerals consisting $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra linked at all corners) can reduce the concentration of heavy metals in contaminated soil (Hettiarachchi *et al.*, 2000). Zeolites are naturally occurring hydrated aluminosilicate inorganic minerals. They are characterised by negative charges which can reduce plant available heavy metals through ion exchange and adsorption processes (Garau *et al.*, 2007). Ion-exchange is considered to be cost-effective due application of abundant and naturally occurring ion-exchangers such as zeolites.

Organic Matter

Organic amendments have also been applied to immobilise heavy metals in contaminated soil through adsorption or complexation (Bolan and Duraisamy, 2003; Shuman, 1998). The organic amendments reported in the literature include municipal biosolids, composts, animal manures and peat and biochars (Ogundiran *et al.*, 2015; Beesley *et al.*, 2011; Adejumo *et al.*, 2011; Farrell and Jones, 2010; Bolan and Duraisamy, 2003). Biochar remediation of heavy metal-contaminated soil is an emerging soil remediation method which employs biological residues combusted under low oxygen conditions, resulting in a porous, low density carbon rich material to decontaminate contaminated soil (Ogundiran *et al.*, 2015; Beesley *et al.*, 2011). Apart from heavy metals immobilization, biochar technique has advantages of carbon sequesteration, little or no CO_2 production when it added to soil, increasing soil pH and soil conditioning properties

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