

Biological, Chemical and Physical Remediation of Heavy Metal Contamination in Soils - A Review

*N. Abdu and Abdullahi, A.A.

Department of Soil Science, Faculty of Agriculture/Institute for Agricultural Research,
Ahmadu Bello University, Zaria, Nigeria

*Corresponding author: nabdu@abu.edu.ng

ABSTRACT

Remediation of heavy metal contaminated soils and related environment is becoming a global challenge. Heavy metal pollution has resulted to several health disorders and death of thousands of people globally, including children, which requires immediate remediation. Biological, chemical and physical technologies of soil remediation including phytoremediation, electro-dialytic and electrokinetic remediation, use of chelating agents, biochar, steaming, excavation, microwaving and infrared radiation have been discussed in the paper. The advantages and disadvantages of each have been highlighted for adoption, depending on circumstances. Sources of heavy metal pollution in soils, its manifestation, risk and harmful effects were also critically reviewed.

Keywords: chelates, electro-dialytic, electrokinetics, soil pollution

INTRODUCTION

Heavy metals are ubiquitous; hence the tendency of environmental pollution with heavy metals is very high. Soil is the basic environmental ecosystem that constitutes elements, and an important material basis for human survival and development. Therefore, it is easily contaminated with heavy metals from various sources from natural to anthropogenic (Li *et al.*, 2010; Yao *et al.*, 2012). Hence, heavy metals in soils are receiving increasing attention due to the greater understanding of their toxicological importance in ecosystems and human health (Hansen *et al.*, 1997).

Global industrialization is the main source of toxic compounds, introducing heavy metals to the biosphere, which constitute a great risk for human health, wild life and the environment (Jing *et al.*, 2007, Pjuelo *et al.*, 2011). Uncontrolled waste disposal and other anthropogenic activities by humans, atmospheric deposition or other natural sources are the main causes of soil contamination with heavy metals (Shazia *et al.*, 2014). Non biodegradability and leaching ability of heavy metals are of particular concern (Shazia *et al.*, 2014).

Several reports of heavy metal contamination that

include a mixture or both organic and inorganic contaminants is becoming widespread, leading to the development of various remediation techniques such as electro-dialytic and electrokinetic remediation (Hansen *et al.*, 1997; Altin and Degirmenci, 2005; Alcántara *et al.*, 2010; Alcántara *et al.*, 2012). Sometimes chelating agents formed from d-block elements, along with other natural chelating agents like citrate that form stable metal complexes and ligands in the soil, are used for heavy metal extraction and subsequent remediation (Huang *et al.*, 1997; Chen *et al.*, 2003).

Likewise, charcoal biomass subjected to pyrolysis under zero or very low oxygen environment, known as biochar, having the properties suitable for carbon sequestration while improving the soil physical, chemical and biological properties has also been employed in heavy metal remediation (Park *et al.*, 2011; Anawar *et al.*, 2015). In the same vein, physical concepts involving replacement of polluted soils through excavation, very deep tillage, moving the contaminants deep inside the soil, importation of clean soil to cover the polluted one or thermal desorption at very high temperatures have also been successfully employed in heavy metal remediation (Yao *et al.*, 2012).

Physical and chemical methods used for remediation of heavy metals suffer from serious limitations such as high cost, intensive labour, alteration of soil properties and disturbance of soil native microorganisms (Ali *et al.*, 2013). Alternatively, organisms and some plant species are employed for the remediation (Khan *et al.*, 2000).

The utilization of organisms including plants and microbes, to clean up contaminated soils, aquifers, sludges, residues and air is known as "bioremediation" (Garbisu and Alkorta, 2003). It has been defined as a remediation strategy which employs plants and microorganisms to remove non-volatile and immiscible soil contaminants (Khan *et al.*, 2000) or the use of green plants to remove environmental contaminants or to render them harmless (Garbisu and Alkorta, 2003). It is also defined as the use of plants and associated soil microbes to reduce the concentration or toxic effects of contaminants in the environment (Ali *et al.*, 2013). Phytoremediation is a rapidly changing and expanding area of environmental biotechnology, offering potentially more effective and economical clean-up technique than the conventional physical and chemical methods (Garbisu and Alkorta, 2003). An emerging technology, which is cost-effective, non-intrusive, aesthetically pleasing, uses the remarkable ability of plants to concentrate elements and compounds from the environment and metabolize various molecules in their tissues (Khan *et al.*, 2000; Alkorta *et al.*, 2004; Jing *et al.*, 2007). It prevents landscape destruction and enhances activities and diversity of soil microorganisms to maintain healthy ecosystems (Jing *et al.*, 2007). Hence, considered more attractive alternative to traditional methods employed for remediation of heavy metals contamination in soils (Jing *et al.*, 2007). This paper therefore, critically examines these biological, chemical and physical methods of remediation through discussion of the mechanisms involved in their application to achieve desired goals and their consequences.

Sources of heavy metal contamination in soils

Heavy metals enter the environment from natural and anthropogenic sources, the most significant natural sources being weathering of minerals, erosion and volcanic activity (Perreiro *et al.*, 2014). Some soils could have a high amount of background heavy metals due to volcanic activity or weathering of parent materials. However, in other soils anthropogenic activities such as mining and smelting of metals, electroplating, gas exhaust, energy and fuel production, fertilizer, sewage sludges and pesticide application, municipal waste generation, industrial discharge, atmospheric deposition, use of biosolids in agriculture etc, are responsible for high level of heavy metals in soils (Jing *et al.*, 2007; Khan *et al.*, 2008; Wuana and Okieime, 2011; Ali *et al.*, 2013; Perreiro *et al.*, 2014).

Generally, industrialization and technological

advances basically led to increase in the use of heavy metals, hence higher heavy metal pollution (Jing *et al.*, 2007, PAZ-Perreiro *et al.*, 2014). Heavy metals usually become contaminants in the soil environments because (i) their rate of generation via man-made cycles are more rapid relative to natural ones, (ii) they become transferred from mines to random environmental locations where higher potentials of direct exposure occur, (iii) the concentrations of the metals in discarded products are relatively higher compared to those in the receiving environment, and (iv) the chemical form (species) in which a metal is found in the receiving environmental system may render it more bioavailable (Wuana and Okieime, 2011).

Manifestation, risks and harmful effects of heavy metal contamination

Pollution of the biosphere by toxic metals is a global threat that has accelerated dramatically since the beginning of the industrial revolution (Khan *et al.*, 2008). Relatively, sudden introduction of pollutants into the recipient ecosystems has clearly overwhelmed their self-cleaning capacity and consequently resulted in their accumulation (Garbisu and Alkorta, 2003). Heavy metals released from these sources accumulate in the soil and in turn, adversely affect the microbial population density, as well as the biological, physical and chemical properties of soils, leading to loss of soil fertility and crop yields (Garbisu and Alkorta, 2003; Khan *et al.*, 2008; Kavamura and Esposito, 2010).

Contamination of the soil with heavy metals may pose risks and hazards to humans and the ecosystem through direct ingestion or contact with the contaminated soil, the food chain (soil-plant-human or soil-plant-animal-human), drinking of contaminated ground water, reduction in the quality of food (safety and marketability) via phytotoxicity, reduction in land usability for agricultural production, causing food insecurity, and land tenure problems (Wuana and Okieime, 2011). Heavy metals are also reported to have adverse effects on human health, causing contamination of the food chain that deserves special attention (Khan *et al.*, 2008; Ali *et al.*, 2013). They cause oxidative stress, which is the enhanced generation of reactive oxygen species (ROS) that can overwhelm the cell's intrinsic antioxidant defenses leading to damage or death (Ali *et al.*, 2013). The same authors also observed the same reason to cause replacement of essential metals in pigments or enzymes disrupting their function. Regarding extent of toxicity, the most problematic heavy metals are Hg, Cd, Pb, As, Cu, Zn, Sn, and Cr (Ali *et al.*, 2013; Kavamura and Esposito, 2010). Mercury, Cd, Pb, and As are non-essential heavy metals while Cu and Zn are essential heavy metals (trace elements). They cause different health problems depending on their concentration and oxidation state (Kavamura and Esposito, 2010; Ali *et al.*, 2013). Ali *et al.*

(2013) elaborated the following specific adverse effects of heavy metals on human health; As is an analogue of phosphate and thus interferes with essential cellular processes such as oxidative phosphorylation and ATP synthesis, Cd is carcinogenic, mutagenic and teratogenic, endocrine disruptor, interferes with calcium regulation in biological systems, causes renal failure and chronic anaemia, Cr causes hair loss, Cu causes brain and kidney damage, liver cirrhosis and chronic anaemia, as well as stomach and intestinal irritation at elevated levels, Hg causes anxiety, autoimmune diseases, depression, difficulty in balance, drowsiness, fatigue, hair loss, insomnia, irritability, memory loss, recurrent infections, restlessness, vision disturbances, tremors, temper outbursts, ulcers and damage to brain, kidney and lungs, Ni causes allergic dermatitis known as nickel itch, inhalation can cause cancer of the lungs, nose and sinuses, cancers of the throat and stomach, while hematotoxic, immunotoxic, neurotoxic, genotoxic, reproductive toxic, pulmonary toxic, nephrotoxic, hepatotoxic and hair loss have also been attributed to its inhalation, Pb poisoning causes problems in children such as impaired development, reduced intelligence, loss of short term memory, learning disabilities and coordination problems, renal failure, increased risk for development of cardiovascular disease and finally Zn over dosage can cause dizziness and fatigue.

Phytoremediation techniques of heavy metal contamination in soils

Phytoremediation is a concept, where living plants are directly used for *in situ* remediation of contaminated soil, sludge, sediments, and ground water through contaminant removal, degradation or containment, involving different techniques. Example of such techniques is phytoextraction (also known as phytoaccumulation, phytoabsorption or phytosequestration), which is the uptake of contaminants from soil or water by plant roots and their translocation and accumulation in aboveground biomass i.e. shoots (Ali *et al.*, 2013). Metal translocation to shoots is a crucial biochemical process and is desirable in any effective phytoextraction because the harvest of root biomass is generally not feasible (Ali *et al.*, 2013). The success of phytoremediation, therefore, depends upon the selection of plant species that maximize the removal of heavy metals from contaminated soils into their shoots, while the contaminant(s) must be within the plants rooting zone, in bioavailable and biologically absorbable forms (Khan *et al.*, 2008).

Phytoremediation is a relatively recent emerging technology and is perceived as cost-effective, efficient, novel, eco-friendly, and solar-driven technology with good public acceptance, employed to remove pollutants from contaminated soils (Alkorta *et al.*, 2004; Khan *et al.*, 2008; Ali *et al.*, 2013). This sustainable and inexpensive

process is emerging as a viable alternative to traditional contaminated land remediation methods (Khan *et al.*, 2000). The efficiency of phytoremediation can be enhanced by the judicious and careful application of appropriate heavy-metal tolerant, plant growth promoting rhizobacteria, including nitrogen-fixing organisms in case of legumes (Khan *et al.*, 2000; Khan *et al.*, 2008).

Techniques/strategies of phytoremediation

Phytoremediation of heavy metals may be conducted using any of the following techniques/strategies; phytoextraction, rhizofiltration (or blastofiltration), phytostabilization, phytovolatilization, phytodegradation, phytostimulation, phytotransformation, rhizodegradation, plant-assisted bioremediation, plant-assisted degradation or plant-aided *in situ* biodegradation. A summary of the description of the techniques is shown in Table 1. Plants used for phytoextraction, i.e., metal removal from soil, should have the following characteristics: (i) tolerance to toxic effect of the target heavy metal (ii) ability to accumulate reasonably high levels of the metal (iii) rapid growth rate (iv) ability to produce reasonably high above ground biomass in the field and (v) widely distributed/ highly branched root system (Garbisu, 2002; Ali *et al.*, 2013). Newly discovered efficient metal hyperaccumulators among plants are being explored for applications in phytoremediation and phytomining, as well molecular tools are being used to better understand the mechanisms of metal uptake, translocation, sequestration and tolerance by these plants (Ali *et al.*, 2013). For instance, water hyacinth (*Eichhorniacrassipes*) is a well-known hyper-accumulator, bioindicator and phytoremediator of nitrogen and metals (Mehmood, 2009). Water hyacinth grown in waste water and soil of landfills may also be associated with some microbes such as *Aspergillusniger*, *Azotobacter*, *Thiobacillusthiooxidans* (*Acidithiobacillusthiooxidans*) and *T. ferrooxidans* (*A. ferrooxidans*) that play a vital role in bioremediation of metals and nitrogenous compounds (Mehmood, 2009). Other examples of hyperaccumulators of heavy metals among plants are shown in Table 2.

Other characteristics of plants suitable for phytoremediation according to Ali *et al.* (2013) include; (i) high accumulation of the target heavy metals from the soil (ii) effective translocation of the accumulated heavy metals from roots to shoots (iii) good adaptation to prevailing environmental and climatic conditions (iv) resistance to pathogens and pests (v) easy cultivation/harvest and (vi) repulsion to herbivores to avoid food chain contamination. A comprehensive list of plant species exhibiting resistance to high dosage of heavy metals commonly referred to as hyper accumulators have been reported by (Abdu *et al.*, 2017). Plants used in phytoremediation of heavy metal include Maize (*Zea mays*), *Mucuna* (*Mucunapruriens*), Okra

(*Abelmoschus esculentus*), and Kenaf (*Hibiscus cannabinus*), where maize > kenaf > mucuna one trial while in another okra > maize > kenaf (Azeez *et al.*, 2013).

Advantages of phytoremediation

Phytoremediation generally offers the possibility to destroy or render harmless, various contaminants using natural biological activity of plants. As such, it is inexpensive, low technology technique, which generally has a high public acceptance and can consistently be carried out on contaminated sites, often without adversely affecting the fertility of soils or the metabolic activities of microbes (Khan *et al.*, 2008). The biological properties and physical structure of the soil is maintained, and the technique is environmentally friendly, potentially cheap, and visually undistruptive and offer the possibility of bio-recovery of the heavy metals (Khan *et al.*, 2000). Other advantages of phytoremediation according to Alkorta *et al.* (2004) are its applicability to the remediation of a wide variety of organic and inorganic contaminants, reduction of the amount of wastes going to landfills, lack of requirement for extensive equipment or highly specialized personnel, possibility of its application *in situ*, reduction of soil disturbance and the spread of contaminants, cheapness over other conventional remediation methods, ease of implementation and the plants also being cheap and renewable resource, easily available, environmental friendliness, aesthetically pleasing, socially accepted, low tech-alternative and less noisy than other remediation methods.

Phytoremediation helps to avoid the transport of waste offsite and consequently avoiding the potential threats to human health and the environment that could arise during transportation. Furthermore, bioremediation could be useful for remediation of variety of contaminants leading to the complete destruction and when the contaminants are transformed/degraded, the toxicity of contaminants declines (Khan *et al.*, 2008).

Likewise, several possible utilizations of biomass after heavy metal extraction have been suggested by researchers. A mixture of producer gas and/or pyro-gas that can be used to generate thermal and electrical energy can be obtained through combustion and gasification of biomass obtained from heavy metal phytoremediation process (Iyer *et al.*, 2002). Bio-ores could be produced by ashing biomass after phytomining of metals; high concentration of heavy metals that are essential to plant growth in the biomass after phytoextraction can be diluted with clean biomass and utilized in formulation of chemical fertilizer (Wuana and Okieime, 2011).

Limitations of phytoremediation

Phytoremediation is not a cure-all technique for contaminated soils; hence before it is regarded as a technically efficient and cost-effective technique on a

commercial scale, some limitations need to be addressed. These include fact that very little is known about the molecular, biochemical and physiological processes that characterize hyper-accumulation. Long duration is required before remediation is achieved; most heavy metal accumulating plants have shallow rooting depth with low biomass production and slow growth rate to allow remediation within a reasonable period (< 5 years) (Khan *et al.*, 2000). Other limitations of the technique are potential contamination of the food chain if animals graze on the heavy metal contaminated plant biomass and the problem of disposal of the potentially hazardous biomass (Khan *et al.*, 2000; Garbisu and Alkorta, 2003). The technique is also climate and season dependent; it could also lose effectiveness when damage occurs to the vegetation by pests and in the case of inappropriate invasive plant species (Alkorta *et al.*, 2004). Moreover, biological processes of remediation are often specific, they require active and specific plants or microbial communities whose success depends on nutrient status of soil, and levels of contaminants in the sites to be remediated (Khan *et al.*, 2008). They are also time-consuming and have problems in transferring experimental success from laboratory to field environment (Khan *et al.*, 2008). Phytoextraction, one of the most encompassing phytoremediation technique requires transdisciplinary (not simply multidisciplinary) approach with inputs from many fields such as botany, plant physiology, biochemistry, geochemistry, agricultural engineering, agronomy, soil science, genetic engineering and so on (Alkorta *et al.*, 2004).

Despite these and other similar limitations, the future of phytoremediation, as a bioremediation technique appears bright, as the advances in the diverse disciplines that shape bioremediation concepts are accelerating (Garbisu and Alkorta, 2003).

CHEMICAL REMEDIATION

Electrodialytic and Electrokinetic remediation

Environmental pollution with heavy metals and polyaromatic hydrocarbons (PAHs) is becoming widespread. These pollutants are a mixture or both organic and inorganic contaminants, making them difficult to remediate with conventional remediation techniques (Maturi *et al.*, 2006) due to the different chemical composition of the pollutants. In recent years, scientist have developed the concept of electrokinetic or electro-dialytic remediation to combat the deleterious effect a combination of organic and inorganic contaminants have on soils and related environments (Hansen *et al.*, 1997; Pederson, 2002; Altin and Degirmenci, 2005; Alcántara *et al.*, 2010, Alcántara *et al.*, 2012). Electro-dialytic soil remediation is closely connected to electrokinetic remediation, and the cleaning

Table 1: Summary of phytoremediation techniques

S/No.	Technique	Description
1	Phytoextraction	Accumulation of pollutants in the soil into harvestable biomass i.e. shoots, roots and subsequent removal (Garbisu and Alkorta, 2003; Alkorta <i>et al.</i> , 2004; Khan, 2005; Kavamura and Esposito, 2010; Ali <i>et al.</i> , 2013).
2	Phytofiltration (rhizofiltration)	Sequestration of pollutants, mostly heavy metals from contaminated waters by using plant roots (rhizofiltration) or seedlings (blastofiltration) (Alkorta <i>et al.</i> , 2004; Ali <i>et al.</i> , 2013).
3	Phytostabilization	Limiting the mobility and bioavailability of pollutants in soil through extraction and precipitation by plant as lignin or soil humus (Alkorta <i>et al.</i> , 2004; Khan, 2005; Kavamura and Esposito, 2010; Ali <i>et al.</i> , 2013).
4	Phytovolatilization	Conversion of pollutants to volatile form and their subsequent release to the atmosphere e.g. uptake and release into the atmosphere of volatile materials such as mercury - or arsenic-containing compounds (Alkorta <i>et al.</i> , 2004; Khan, 2005; Kavamura and Esposito, 2010; Ali <i>et al.</i> , 2013).
5	Phytodegradation (phytotransformation)	Degradation of organic xenobiotics by plant enzymes within plant tissues (Alkorta <i>et al.</i> , 2004; Ali <i>et al.</i> , 2013).
6	Rhizodegradation	Degradation of organic xenobiotics in the rhizosphere by rhizospheric microorganisms (Khan <i>et al.</i> , 2005; Kavamura and Esposito, 2010; Ali <i>et al.</i> , 2013).
7	Phytodesalination	Removal of excess salts from saline soils by halophytes (Ali <i>et al.</i> , 2013).
8	Phytostimulation	The use of plant roots in conjunction with their rhizospheric microorganisms to remediate soils contaminated with organics (Alkorta <i>et al.</i> , 2004; Kavamura and Esposito, 2010).
9	Plant-assisted bioremediation	Plant-assisted degradation, plant aided <i>in situ</i> biodegradation (Alkorta <i>et al.</i> , 2004).
10	Rhizofiltration	Use terrestrial plants to absorb, concentrate and/or precipitate contaminants in the aqueous system (Kavamura and Esposito, 2010).

Table 2. Examples of hyperaccumulators among plants and the heavy metals they accumulate

S/No.	Metal species	Plants
1	Zinc (Zn)	<i>Thiobacilluscaerulescens</i>
2	Cadmium (Cd)	<i>Thiobacilluscaerulescens</i>
3	Nickel (Ni)	<i>Berkheyacoddii</i>
4	Selenium (Se)	<i>Astragalusracemose</i>
5	Thallium (Tl)	<i>Iberisintermedia</i>
6	Copper (Cu)	<i>Ipomoea alpine</i>
7	Cobalt (Co)	<i>Haumaniastrumrobertii</i>
8	Arsenic (As)	<i>P. vittata</i>

Source: (Alkorta *et al.*, 2004).

agent of both methods is an electric current that is applied to the soil. The two methods only differ in the separation between the soil and the electrode compartments. In electrokinetic remediation, passive barriers are used whereas in electrodialytic remediation, ion-exchange membranes are used (Heidari *et al.*, 2011). Both techniques, however, involve the use of electric energy to ionize the contaminants such as heavy metals in a sample such that the ionized contaminants will migrate towards the direction of the electrodes via electrostatic attraction. The mechanism of electrokinetic remediation involves transportation of the pollutants through electromigration, electrophoresis and electro-osmosis (Albergaria *et al.*, 2006; Traina *et al.*, 2007; Xiu and Zhang, 2009; Alcántara *et al.*, 2012). The pollutant is carried to two poles treatment room via electromigration, electro-osmotic flow or electrophoresis and then treated further (Yao *et al.*, 2012). Movement of ions in an electric field is referred to as electromigration; movements of liquid in a soil pore relative to the charged particles in the soil solution. The techniques involves application of electric field which produces a force on the thin layer of a charged fluid, which counterbalances the surface charge, resulting in a net migration of ions in one direction within the fluid (Hansen *et al.*, 1997). Electrophoresis is the movement of charged colloidal particles relative to the liquid in the applied electric field (Hansen *et al.*, 1997). Electrokinetic remediation has been demonstrated to be environmentally friendly, has multifunctional adaptability and sustainable (Li *et al.*, 2013). The heavy metal pollutant is finally removed from the electrode by precipitation.

Electrokinetic remediation and bioleaching of heavy metals from contaminated environments are sometimes combined in a process known as bioelectrokinetics (Maini *et al.*, 2000, Lee *et al.*, 2009; Kim *et al.*, 2012). Likewise, bacteria such as *A. ferrooxidans* are sometimes inoculated into the electrolyte in the process of bioelectrokinetics to improve the removal efficiency of heavy metals (Kim *et al.*, 2012). The role of the bacteria is to immobilize the heavy metals within the electrolytic environment, thus involving bioremediation to some extent (Kim *et al.*, 2012).

Using chelating agents as facilitators of remediation

A chelate is composed of a metal ion and a chelating agent, which can form several bonds to a single metal ion, sometimes forming strong, water soluble metal complexes with di- and trivalent cations (Shazia *et al.*, 2014). Most of the d-blocks elements in the periodic table comprising of mostly heavy metals and transitional elements have the capability of forming large variety of complexes and chelates. Chelating agents that form stable metal complexes and ligands in the soil and used for heavy metal extraction are known as aminopolycarboxylates (APCA). These include Ethylene di amine tetra acetic acid (EDTA), hydroxyethyl ethylene-diamine tri acetic acid

(HEDTA), di ethylene tri amine penta acetic acid (DTPA) and ethylene di amine di (o-hydroxy phenyl acetic acid (EDDHA) (Huang *et al.*, 1997). These and other natural chelating agents like citrate that forms stable chelates with heavy metals have been largely employed in heavy metal extraction from contaminated soils (Wasay *et al.*, 1998; Luo *et al.*, 1999; Pedersen, 2002; Chen *et al.*, 2003; Nowack, 2007). Application of chelating agents to the soil can bring metals into solution through desorption of sorbed species, dissolution of Fe and Mn oxides, and dissolution of precipitated compounds (Shazia *et al.*, 2014). Chelating agents are also used to improve the efficiency of phytoremediation, a process known as chelate-induced phytoextraction. This is achieved by the formation of metal-chelate complex which is taken up by the plant and transported through a passive apoplastic pathway (Wuana and Okieime, 2011, Shazia *et al.*, 2014). Addition of a chelating agent (EDTA) to a Pb-contaminated soil increased shoot Pb concentration of *Zea mays* L. and *Pisum sativa* from < 500 mgkg⁻¹ to > 10,000 mgkg⁻¹ (Maini *et al.*, 2000).

New generation complexing agents used in remediation of soil contaminants include IDS (N-(1, 2-dicarboxyethyl)-D, L-aspartic acid (imino di succinic acid), DS (poly aspartic acid), EDSS (N,N'-ethylene diamine di succinic acid), GLDA (N,N-bis(carboxyl methyl)-L-glutamic acid) and MGDA (methyl glycine di acetic acid) (Kołodziejńska, 2013). All of these are eco-friendly, with the exception of IDS or EDSS that their biodegradability depends on their isomeric forms (Knepper, 2003; Kołodziejńska, 2013).

Chemical fixation of heavy metals in polluted soils has also been demonstrated to be effective in reducing soil-metal pollution (Zhou *et al.*, 2004; Yao *et al.*, 2012). This remediation technique involves the use of materials such as clays, metallic oxides, biomaterials, phosphate rock or apatite (Ca₁₀(PO₄)₆OH₂), furfural dreg and weathered coal (Hodson and Valsami-Jones, 2000; Zhang *et al.*, 2009). Natural and synthetic zeolites (Barakat, 2011, Nah *et al.*, 2006), activated phosphate (Pan *et al.*, 2007), hydrous titanium oxide (Ghosh *et al.*, 2003; Barakat, 2005), manganese-modified natural sand (Tiwari *et al.*, 2011) have all been used in the removal of heavy metals from contaminated environments. Therefore, chelates have confirmed potential for the remediation of heavy metal-contaminated soils either as on-site soil washing agents or for in-situ remediation (Shazia *et al.*, 2014). Chelating agents are the most popular extracting reagents for soil washing, since chelating agents such as EDTA, EDSS, DTPA and NTA form stable complexes with most heavy metals over a broad pH range, hence proved to be the most efficient (Heidari *et al.*, 2011). The main disadvantage of the technique is alteration of the bioavailability of heavy

metals in the soils due to changing chemical condition of the soil, making the heavy metal more mobile, even though, it has been used effectively (Bolan *et al.*, 2003). The added chemicals may also reduce the activities of the soil microbial biomass (Yao *et al.*, 2012). The disadvantages of the technique also include persistence in the environment (particularly EDTA), adverse health effects (particularly NTA) and high cost (particularly EDDS) which has sometimes precludes their use in remediation of metal contaminated sites (Heidari *et al.*, 2011).

ROLE OF BIOCHAR IN FACILITATING REMEDIATION

Biochar is a charcoal biomass subjected to pyrolysis under zero or very low oxygen environment. It has the properties of sequestering carbon and at the same time improving soil physical, chemical and biological properties (Park *et al.*, 2011; Anawaret *et al.*, 2015), that is devoid of short and long-term environmental hazards and adverse health effects on the ecosystem (Verheijen *et al.*, 2010). It has been widely employed in the remediation of soils polluted with both organic and inorganic pollutants such as heavy metals. Properties of biochar such as highly porous structure, composition of numerous and diverse functional groups and high surface area makes it very effective in remediation of heavy metals and other organic soil pollutants like PAHs (Liu and Zhang, 2009). Park *et al.* (2011) reported immobilization of Cd, Cu and Pb and reduced uptake of these metals by *Brassica juncea* as a result of biochar amendment. They also observed biochar to modify the partitioning of these heavy metals from the readily available fraction to the less bioavailable organic fractions. High sorption of Zn and Cd by biochar and decreased Zn concentration in the leachate of biochar amended soils has been reported (Novak *et al.*, 2009; Laird *et al.*, 2010; Beesley and Marmiroli, 2011).

Perhaps, the most important disadvantages of biochar are the cost, technical requirements and emissions from production process. Biochar production is associated with the emission of atmospheric pollutants (e.g. PAHs, dioxins) and particulate matter, therefore the need for tight control on the feedstock materials and pyrolysis conditions to reduce them (Verheijen *et al.*, 2010). Similarly, the production is associated with implications to human health, which are mainly related to occupational hazard and lack of robust qualitative and quantitative assessment of such emissions from pyrolysis of traditional biomass feedstock (Verheijen *et al.*, 2010).

PHYSICAL REMEDIATION

Remediating heavy metal-contaminated soils relies heavily on 'dig-and-dump' or encapsulation, neither of which addresses the issue of decontamination of the soil (Pulford and Watson, 2003). Physical remediation of

heavy metal contaminated soils involves replacement of the polluted soil through excavation, soil spading involving very deep tillage and moving the contaminant deep into the soil or importation of clean soil to cover the polluted one (Yao *et al.*, 2012). These methods were employed by the Blacksmith Institute in remediation of Pb polluted soils in northern Nigeria (Abdu *et al.*, 2007). Another physical method of soil remediation is thermal desorption, involving volatilization of the pollutant through steaming, microwaving and infrared radiation (Yao *et al.*, 2012). This is carried out under high temperature ranging from 90°C to over 500°C during which the heavy metal is volatilized and the volatile heavy metal pollutants are then removed via vacuum negative pressure or carrier gas.

These physical methods of soil remediation could, however, be very expensive, time demanding and could possibly lead to contamination of the site to which the polluted soil is moved to (Yao *et al.*, 2012). Incorporating the pollutants deep inside the soil may increase the risk of underground water contamination through leaching (Yao *et al.*, 2012). Another technique is immobilization or extraction by physical and chemical techniques, which could also be expensive and often appropriate only for small areas where rapid, complete decontamination is required. Similarly, methods, such as soil washing, have adverse effect on biological activity, soil structure and fertility, while others require significant engineering costs (Laird *et al.*, 2010).

CONCLUSION

Heavy metals from natural and anthropogenic sources cause environmental and soil pollution resulting in adverse agricultural and human health risks. This paper discussed biological, chemical and physical techniques for combating heavy metal pollution, which include; electro-dialytic/electrokinetic remediation, facilitation of remediation using chemical factors such as chelating agents and biochar. Physical remediation techniques have also been highlighted, offering options for adoption, as may be dictated by circumstances. Among the remediation techniques discussed is biological remediation, particularly, phytoremediation of heavy metals contamination, which is a fascinating technique with potential for wide application. It involves various ways of employing the remarkable ability of plants to remove heavy metal pollutants from the environment. It is indeed a potential booming industry for soil and environmental remediation from heavy metal contamination.

REFERENCES

- Abdu, N. Abdulkadir, A. and Abdullahi, A.A. (2017). Heavy metals and soil microbes. *Environmental Chemistry Letters* **15**(1): 65-84.
- Ali, H. Khan, E. and Sajad, M.A. (2013). Phytoremediation of heavy metals - Concepts and applications. *Chemosphere* **91**:869-881.
- Albergaria, J. T., da Conceicao, M., Alvim-Ferraz, M. and Delerue-Matos, C. (2006). Remediation efficiency of vapour extraction of sandy soils contaminated with cyclohexane: Influence of air flow rate, water and natural organic matter content. *Environmental Pollution* **143**: 146-152.
- Alcántara, M. T., Gómez, J., Pazos, M. and Sanromán, M. A. (2012). Electrokinetic remediation of lead and phenanthrene polluted soils. *Geoderma* **173-174**: 128-133.
- Alcántara, M. T., Gómez, J., Pazos, M., Sanromán, M. A. (2010). Electrokinetic remediation of PAH mixtures from kaolin. *Journal of Hazardous Materials* **179**: 1156-1160.
- Alkorta, J.H., Becerril, J.M., Amezaga, I., Albizu, I. and Garbisu, C. (2004). Recent findings on the phytoremediation of soils contaminated with environmentally toxic heavy metals and metalloids such as zinc, cadmium, lead, and arsenic I. *Review of Environmental Science and Biotechnology* **3**:71-90.
- Altin, A. and Degirmenci, M. (2005). Lead (II) removal from natural soils by enhanced electrokinetic remediation. *Science of the Total Environment* **337**: 1-10.
- Anawar, H. M, Akter, F., Solaiman, Z. M, and Strezov, V. (2015). Biochar: an emerging panacea for remediation of soil contaminants from mining, industry and sewage wastes. *Pedosphere* **25**(5):654-665.
- Azeez, J. O., Hassan, O. A., Adesodun, J. K. and Arowolo, T.A. (2013). Soil Metal Sorption Characteristics and its Influence on the Comparative Effectiveness of EDTA and Legume Intercrop on the Phytoremediative Abilities of Maize (*Zea mays*), Mucuna (*Mucunapruriens*), Okra (*Abelmoschus esculentus*), and Kenaf (*Hibiscus cannabinus*), *Soil and Sediment Contamination: An International Journal* **22**(8): 930-957.
- Barakat, M. A. (2005). Adsorption behavior of copper and cyanide ions at TiO₂-solution interface. *Journal of Colloid Interface Science* **291**: 345-352.
- Bolan, N. S., Adriano, D. C., Duraisamy, P. (2003). Immobilization and phytoavailability of cadmium in variable charge soils. III. Effect of biosolid compost addition. *Plant and Soil* **256**(1): 231-41.
- Barakat, M. A. (2011). New trends in removing heavy metals from industrial wastewater. *King Saud University Arabian Journal of Chemistry* **4**:361-377.
- Chen, Y. X., Lin, Q., Luo, Y. M., He, Y. F., Zhen, S. J., Yu, Y. L., Tian, G. M. and Won, M. H. (2003). The role of citric acid on the phytoremediation of heavy metal contaminated soil. *Chemosphere* **50**:807-811.
- Garbisu, C. and Alkorta I. (2003). Basic concepts on heavy metal soil bioremediation. *European Journal of Mineral Processing and Environmental Protection* **3**(1): 58-66.
- Garbisu, C., Hernández-Allica, J., Barrutia, O., Alkorta, I., and Becerril, J.M. (2002). Phytoremediation: a technology that uses green plants to remove contaminants from polluted areas. *Reviews on Environmental Health* **17**(3): 173-188.
- Gavrilescu, M. (2004). Removal of heavy metals from the environment by biosorption. *Engineering in Life Sciences* **4**(3):219-232.
- Ghosh, U. C., Dasgupta, M., Debnath, S. and Bhat, S. C. (2003). Studies on management of chromium(VI)-contaminated industrial waste effluent using hydrous titanium oxide (HTO). *Water, Air and Soil Pollution*. **143**: 245-256.
- Hao, X. Taghavi, S. Xie, P., Orbach, M.J., Alwathnani, H.A., Rensing, C. and Wei, G. (2014). Phytoremediation of heavy and transition metals aided by legume-rhizobia symbiosis. *International Journal of Phytoremediation*, **16**:179-202.
- Hansen, H. K., Ottosen, L. M., Kliem, B. K. and Villumsen, A. (1997). Electrodialytic Remediation of Soils Polluted with and Cu, Cr, Hg, Pb and Zn. *Journal of Chemistry Technology and Biotechnology* **70**: 67-73.
- Heidari, O. S., Neyshabouri, M. R., Reyhanitabar, A., Bybordi, A. (2011). Removal of heavy metals from a contaminated calcareous soil using oxalic and acetic acids as chelating agents. *International Conference on Environment Science and Engineering, IPCBEE* Vol.8. IACSIT Press, Singapore. 152-155.
- Hodson, M, E., Valsami-Jones, É. (2000). Bone meal additions as a remediation treatment for metal contaminated soil. *Environmental Science and Technology* **34**(16): 3501-7.

- Huang, J. W., Chen, J. J., Berti, W. R. and Cunningham, S. D. (1997). Phytoremediation of lead-contaminated soils: Role of synthetic chelates in lead phytoextraction. *Environmental Science and Technology* **31**: 800-805.
- Iyer, P.V.R., Rao, T.R. and Grover, P.D. (2002). Biomass Thermochemical Characterization, Indian Institute of Technology, Delhi, India, 3rd edition.
- Jing, Y., He, Z. and Yang, X. (2007). Role of soil rhizobacteria in phytoremediation of heavy metal contaminated soils. *Journal of Zhejiang University of Sciences B.*, **8**(3):192-207.
- Kavamura, V.N. and Esposito, E. (2010). Biotechnological strategies applied to the decontamination of soils polluted with heavy metals. *Biotechnology Advances*, **28**:61-69.
- Khan, A.G. (2005). Role of soil microbes in the rhizospheres of plants growing on trace metal contaminated soils in phytoremediation. *Journal of Trace Elements in Medicine and Biology*, **18**:355-364.
- Khan, A.G., Kuek, C., Chaudhry, T.M., Khoo, C.S. and Hayes, W.J. (2000). Role of plants, mycorrhizae and phytochelators in heavy metal contaminated land remediation. *Chemosphere*, **41**:197-207.
- Khan, M.S., Zaidi, A., Wani, P.A. and Oves, M. (2008). Role of plant growth promoting rhizobacteria in the remediation of metal contaminated soils. *Environmental Chemistry Letters*, **7**:1-19.
- Kim, H. A., Lee, K. Y., Lee, B. T., Kim, S. O. and Kim, K. W. (2012). Comparative study of simultaneous removal of As, Cu, and Pb using different combinations of electrokinetics with bioleaching by *Acidithiobacillus ferrooxidans*. *Water Resources* **46**:5591-5599.
- Knepper, T. P. (2003). Synthetic chelating agents and compounds exhibiting complexing properties in the aquatic environment. *Trends in Analytical Chemistry* **22**:708-724.
- Kołodźńska, D. (2013). Application of a new generation of complexing agents in removal of heavy metal ions from different wastes. *Environmental Science and Pollution Research* **20**:5939-5949. DOI 10.1007/s11356-013-1576-2.
- Laird, D., Fleming, P., Wang, B., Horton, R. and Karlen, D. (2010). Biochar impact on nutrient leaching from a Midwestern agricultural soil. *Geoderma*, **158**:436-442.
- Lebrazi, S. and Fikri, B. K. (2014). Environmental stress conditions affecting the N₂ fixing *Rhizobium-legumes* symbiosis and adaptation mechanisms. *African Journal of Microbiology Research*, **8**(53):4053-4061.
- Lee, K. Y., Yoon, I. H., Lee, B. T., Kim, S. O. and Kim, K. W. (2009). A novel combination of anaerobic bioleaching and electrokinetics for Arsenic removal from mine tailing soil. *Environmental Science and Technology* **43**: 9354-9360.
- Li, D. W., Huang, T. and Yang, K. (2013). Research on the experiment of electrokinetic remediation of the municipal solid waste incineration fly ashes based on orthogonal method. *Research Journal of Chemistry and Environment* **17**: 53-59.
- Luo, Y. M., Christie, P. and Baker, A. J. M. (1999). Metal uptake by *Thlaspi caerulescens* and metal solubility in a Zn/Cd contaminated soil after addition of EDTA. In Proceedings of the Fifth International Conference on the Biogeochemistry of Trace Elements, Vienna, Austria, 2, pp. 882-883.
- Maini, G, Sharman, A. K, Sunderland, G., Knowles, C. J and Jackman, S. A. (2000). An integrated method incorporating sulfur-oxidizing bacteria and electrokinetics to enhance removal of copper from contaminated soil. *Environmental Science and Technology* **34**:1081-1087.
- Maturi, K. and Reddy, K. R. (2006). Simultaneous removal of organic compounds and heavy metals from soils by electrokinetic remediation with a modified cyclodextrin. *Chemosphere*, **63**:1022-1031.
- Mehmood, T., Malik, S.A. and Hussain, S.T. (2009). Role of microbes in nitrogen and metal hyperaccumulation by taxilaion *Eichhorniacrassipes*. *African Journal of Microbiology Research*, **3**(12):914-924.
- Nah, I. W., Hwang, K. Y., Jeon, C. and Choi, H. B. (2006). Removal of Pb ion from water by magnetically modified zeolite. *Mineralogical Engineering* **19** (14): 1452-1455.
- Nowack, B. 2007. Chelating agents – overview and historical perspective. In Nowack, B and Giger, W. (eds.) Complexing agents between science, industry, authorities and users. Monte Verità, Ascona, Switzerland.
- Pan, B. C., Zhang, Q. R., Zhang, W. M., Pana, B. J., Dua, W., Lv, L., Zhanga, Q. J., Xua, Z. W., Zhang and Q. X. (2007). Highly effective removal of heavy metals by polymer-based zirconium phosphate: a case study of lead ion. *Journal of Colloid Interface Science* **310**: 99-105.
- Park, J. H., Choppala, G. K., Bolan, N. S., Chung, J. W. and Chuasavathi, T. (2011). Biochar reduces the bioavailability and phytotoxicity of heavy metals. *Plant Soil* **348**:439-451.

- Paz-Perreiro, J., Lu, H., Fu, S., Méndez, A. and Gascó, G. (2014). Use of phytoremediation and biochar to remediate heavy metal polluted soils: A review. *Solid Earth*, **5**: 65-75.
- Pazos, M., Cameselle C. and Sanroman, M. A. (2008). Remediation of dye-polluted kaolinite by combination of electrokinetic remediation and electrochemical treatment. *Environmental and Engineering Sciences* **25**:419-428.
- Pedersen, A. J. (2002). Evaluation of assisting agents for electrochemical removal of Cd, Pb, Zn, Cu and Cr from MSWI fly ash. *Journal of Hazardous Materials, B* **95**:185-198.
- Pjuelo, E., Rodríguez, I.D., Lafuente, A. and Caviedes, M.A. (2011). Legume-Rhizobium symbiosis as a tool for bioremediation of heavy metal polluted soils. In: M.S. Khan, *et al.* (eds). Bio management of Metal Contaminated Soils, Environmental Pollution 20. Springer Science + Business Media B.V.
- Pulford, I. D. and Watson, C. (2003). Phytoremediation of heavy metal-contaminated land by trees -a review. *Environment International*, **29**, 529-540.
- Rajendran, P., Muthukrishnan, J. and Gunasekaran P. (2003). Microbes in heavy metal remediation. *Indian Journal of Experimental Biology*, **41**:935-944.
- Shazia, A. Shazia, I and Mahmood, U. (2014). Effect of chelating agents on heavy metal extraction from contaminated soils. *Research Journal of Chemical Sciences*, **4**(9), 70-87.
- Tiwari, D., Laldanwngliana, C., Choi, C-H. and Lee, S. M. (2011). Manganese-modified natural sand in the remediation of aquatic environment contaminated with heavy metal toxic ions. *Chemical Engineering Journal* **171**:958-966.
- Traina, G., Morselli, L. and Adorno G. P. (2007). Electrokinetic remediation of bottom ash from municipal solid waste incinerator. *Electrochimica Acta*, **52**:3380-3385.
- Valls, M. and De Lorenzo, V. (2002). Exploiting the genetic and biochemical capacities of bacteria for the remediation of heavy metal pollution. *FEMS Microbiology Review*, **26**:327-338.
- Verheijen, F., Jeffery, S., Bastos, A. C., Vander Velde, M. and Diafas, I. (2010). Biochar Application to Soils A Critical Scientific Review of Effects on Soil Properties, Processes and Functions. EUR 24099 EN, Office for the Official Publications of the European Communities, Luxembourg, 149 pp.
- Wasay, S. A., Barrington, S. F. And Tokunaga, S. (1998). Remediation of soils polluted by heavy metals using salts of organic acids and chelating agents. *Environmental Technology* **19**(4): 369-380.
- Wu, J., Hsu, F. C. and Cunninham, S. D. (1999). Chelate-assisted Pb phytoextraction: Pb availability, uptake, and translocation constrains. *Environmental Science and Technology* **33**:1898-1904.
- Wuana, R.A. and Okieime, F.E. (2011). Heavy Metals in Contaminated Soils: A review of sources, chemistry, risks and best available strategies for remediation. *ISRN Ecology*, 402647:20 doi:10.5402/2011/402647.
- Xiu, F. R. and Zhang, F. S. (2009). Electrokinetic recovery of Cd, Cr, As, Ni, Zn and Mn from waste printed circuit boards: Effect of assisting agents. *Journal of Hazardous Materials*, **170**:191-196.
- Yao, Z., Li, J., Xie, H. and Yu, C. (2012). Review on remediation technologies of soil contaminated by heavy metals. The 7th International Conference on Waste Management and Technology. *Procedia Environmental Sciences*, **16**:722-729.
- Zhang, L. J., Zhang Y., and Liu, D. H. (2009). Remediation of soils contaminated by heavy metals with different amelioration materials. *Soils*, **41**(3):420-4.
- Zhou, D. M., Hao, X. Z. and Xue, Y. et al. (2004). Advances in remediation technologies of contaminated soils. *Ecological and Environmental Science*. **13** (2):234-42.