Chapter **4**

Heavy metal mobility in surface water and soil, climate change, and soil interactions

Opeyemi A. Oyewo, Amos Adeniyi, Mokgadi F. Bopape and Maurice S. Onyango

Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, Pretoria, South Africa

CHAPTER OUTLINE

4.1 INTRODUCTION

Heavy metals contamination is a serious environmental problem due to their persistence in the environment and nonbiodegradable nature leading to their accumulation up to toxic levels. However, the term "heavy metals" refers to any relatively dense and high atomic weight metals, and they are also known for their potential toxicity in environmental contexts. The term heavy metal is applied to cadmium, mercury, lead, arsenic, and all of which appear in the World Health Organization's list of 10 chemicals of major public concern (Chavan et al., 2016). Heavy metals (HMs) found in a certain mining site depends on the type of ores discovered; however, South Africa is well known to be resourced in these minerals for industrialization improvement. Furthermore, the presence of HMs in the environment might be due to the industrial effluent that flows directly into the water system or through the contaminated soils, percolates, which changes the concentration of the underground water systems. However, their health and environmental effects through any sources cannot be overlooked.

The mobility of these metals from one location or state to another is a critical issue to be considered to address this problem from the root. The mobility, bioavailability, and toxicity of metals are influenced by their interactions with phyllosilicates, organic matter, variable charge minerals, and microorganisms (Acosta et al., 2011). The contamination risk of other environmental compartments in soil and water science, the proportion of metals that enter the circulation during mobilization, and the toxicity of a certain heavy metal determine the extent of their active effect on the environment at a particular location. As such, climatic change is another phenomenon that usually affects the mobility and bioavailability of heavy metals in the soil. It has been reported that the increase in temperature enhanced the remobilization processes; this effect may even be stronger in disturbing the natural balance in the environment. Therefore, regular research on the environmental fate of pollution is required, especially in terms of the remobilization of heavy metals from the source (Potapowicz et al., 2018).

The kind of chemicals formed from metals in soils and water could be one of the criteria to evaluate or trace their mobility and bioavailability. To achieve early warning and prevent soil quality from deteriorating, it is necessary to select suitable indices to diagnose heavy metal pollution. However, physicochemical processes influencing the chemistry of metals in soil and water include sorption/desorption, solution complexation, oxidation—reduction; precipitation—dissolution reactions, microbiological indices, chemical speciation, and sequential extraction have been used for the removal of heavy metals from soil and water. For example, sequential extraction tests have been used for assessing trace elements mobility and phytoavailability, while chemical speciation of toxic elements is achieved via spectroscopic analyses (XAS), which provide information about the oxidation state, symmetry, and identity of the coordinating ligand environment, and possible solid phases.

Studies related to heavy metals mobility are scattered, and a critical review is imperative. Therefore, this chapter is mainly to provide readers with an in-depth understanding of the merits and limitations of heavy metals contaminated through mobility in surface water and soil, as well as their remediation. The effect of climate change on soil interactions is also critically discussed. The details of all the current and novel techniques used to minimize the effects of heavy metals in the environment are equally discussed.

4.2 SOURCES OF HEAVY METALS

Heavy metals originated majorly from mining operations and other industries in which their usage is paramount. Mining operations, unlike other sectors, are fully reliant on the location of minerals with limited options to mitigate and adapt to regional water or quality impacts (Akinwekomi et al., 2016). Therefore, the greatest threat posed to water resources and soil science arises from mine discharges that have been found to be contaminated with heavy metals. The presence of heavy metals (iron and sulfate) in mine environment is inevitable due to the saturation of their ores worldwide, especially in South Africa. Other common metals that can be found in mine locations are Cd, V, Cu, Al, Cr, Hg, Pb, Zn, and Ni. As such, the increase in industrialization and urbanization has constantly increased the demand for these metals, as they are mostly base materials in some productions. Some of them are used for pharmaceutical purposes, steel manufacturers, petroleum industry, and electron acceptors and as additives to improve goods production. As the mining and usage of these

metals increases, more risk is being posed to the environment. This thus increases the extent of these toxic metals mobility and bioavailability in the environment.

4.3 HEAVY METALS OF SERIOUS CONCERN

Constant evaluation by many regulation agencies is due to some heavy metals that continually exceed the allowable concentration upon discharge despite all the efforts made by researchers to get rid of them in the environment. However, the adverse effect of all heavy metals is enormous especially when consumed in water or food. Thus the current reviews on the assessment of HMs in soil and surface water bodies throughout the world from 1994 to 2019 are ongoing by WHO to ascertain the type of metals that are difficult to eradicate in the environment. To achieve this goal, multivariate analyses were applied in many cases to determine the possible sources of these HMs. Among the analyzed HMs in a total of 147 publications, the average content of Cr, Mn, Co, Ni, As, and Cd exceeded the permissible limits suggested by WHO and USEPA. Results revealed that the heavy metal pollution index, evaluation index, the degree of contamination, water pollution, and toxicity load showed that the examined water bodies are highly polluted by HMs. The results of the median lethal toxicity index showed maximum toxicity in As, Co, Cr, and Ni in the surface water bodies. Results of ingestion and dermal pathways for adults and children in the analysis showed that As is the major contaminant. Moreover, Cr, Ni, As, and Cd showed values that could be considered as a high risk for cancer generation via the ingestion pathway as compared to the dermal route. It is recommended that remediation techniques such as the introduction of aquatic phytoremediation plant species and adsorbents should be included in land management plans to reduce human risks (Kumar et al., 2019). Tanveer and Wang (2019) reported the toxicity of Beryllium in humans and water and in the soil through crop production. In plants, only a few studies have documented the toxic effects of beryllium. Moreover, plant products (fruits, grains, or other plant parts) could be a major source of beryllium toxicity in our food chain; therefore, it is more imperative to understand how plants can be developed more tolerant to beryllium toxicity. Tanveer and his coworkers primarily highlighted and speculated different beryllium uptake, translocation, and beryllium storage mechanism in plants. It therefore provides considerable information for people who are working in identifying and developing heavy metal hyperaccumulator plants. This also provides

early warning and prevents soil quality from deteriorating due to their persistence in the environment and the nonbiodegradable nature that could lead to their accumulation to toxic levels (Abou-Aly et al., 2019; Hu et al., 2019; Na et al., 2019; Tang et al., 2019; Xavier et al., 2019).

4.4 MOBILITY AND BIOAVAILABILITY OF HEAVY METALS IN THE ENVIRONMENT

Nowadays, a different investigation has shown that the nature and properties of HMs have an important role in determining the type of soil that could accommodate them. Mousavi et al. (2018) investigated the mobility of heavy metals in sandy soil after application of composts produced from maize straw, sewage sludge, and biochar. It was reported that the role of the soil properties and soil condition on the metals' chemical behavior via biosolids application have a duplicate role in trace metals mobility. However, the metals' status in the plant tissues presents valuable information to the scientists and for the interpretation of the organic compound measurements in the soil. For instance, fractionalization of four heavy metals (Cu, Zn, Cd, and Pb) in soils from 10 contaminated cocoa plantations across Ondo State, Nigeria was investigated. Six different operationally defined pools such as water-soluble, extractable, carbonate, Fe−Mn oxide, organic, and residual were reported. The organic fraction was the most abundant pool for copper and zinc, extractable fraction for lead and residual for cadmium. Mobility and bioavailability of these four metals in the studied soils were in the following order: $Pb > Zn > Cd > Cu$. This indicates that lead had the highest chance of being accumulated in cocoa beans (ref). Bioavailability of HMs in surface and underground waters is basically via industrial effluent that flows directly into the water system or is absorbed by the soils, percolates, and then changes the concentration of the underground water systems (Feng et al., 2019). Although the attention has been shifted to effluent treatment lately, the presence of these metals in the river is the indication for further studies. Sulfate, for instance, is highly soluble and mobile and hence its removal is a very tedious task (Tolonen et al., 2016). The consumption of drinking water containing sulfate concentrations in excess of $600 \, \mathrm{mg \, L^{-1}}$ commonly results in laxative effects; therefore, the allowable sulfate concentration in drinking water has been reported to be between 250 and $500 \, \mathrm{mg \, L^{-1}}$ due to its lower environmental risk compared to other dissolved metals. This has been under investigation and in many practices, and little or no useful information has been documented.

4.4.1 Assessment of heavy metals mobility on soil type

Several studies have been conducted on the mobility of HMs on soil components. For example, the mobility of humic acids, polycyclic aromatic hydrocarbons, and coexisting metals is examined on clay minerals using the desorption process. Three types of artificially blended clay and clay mineral mixtures such as pure kaolinite, kaolinite + sand, and kaolinite + sand + bentonite were investigated. Different amounts of humic acid content, polycyclic aromatic hydrocarbons, and HMs were tested by using three extracted solutions $CaCl_2$ (0.01 M) and ethylenediaminetetraacetic acid (EDTA) (0.01 M) with nonionic surfactants (Tween 80 and Triton X100). The study of the mobility of Ni, Pb, and Zn was prioritized in the study. However, the influence of copresent metals on simultaneous desorption and mobility of polycyclic aromatic hydrocarbons (PAHs) was also investigated. It was reported that <10% of metals in the clay mineral mixtures were mobile and combination of EDTA and nonionic solutions can enhance the desorption and mobility of PAHs to >80% in clay mineral mixtures containing no sand, while in some soils containing ~40% of sand, the desorption exceeded 90%. Heavy metals, as well as increasing humic acid content in the clay mineral mixtures, decreased the desorption and mobility of PAHs, especially for soils containing no sand (Saeedi et al., 2018). Another study reported the effect of salinity on HMs' mobility on the soil type. The salinity induced by $CaCl_2$, $MgCl_2$, NaCl, and Na_2SO_4 on the mobility of Cu, Cd, Pb, and Zn was thoroughly investigated. An increase of ionic strength by any salts promoted a higher release of Cd than the other metals. When $CaCl_2$ and NaCl were applied, Cd and Pb showed the highest degree of mobilization in sandy soil. As the total heavy metal content was higher, the percentage of Pb and Cu released upon salinization decreased, indicating that these metals are strongly bound to soil constituents. An increase of carbonates in the soil promoted a higher release of Pb for all used salts and for Zn when $MgCl_2$ and NaCl were used. This indicates that Pb and Zn are adsorbed on the surface of carbonate crystals. An increase of fine particles promoted a decrease in the percentage of released Cd for all salts, indicating that Cd is strongly retained in the soil fine fractions (Acosta et al., 2011). Wu et al. (2015) reported the impact of heavy metal mobility in Haihe River sediments when constructing tide gates in the brackish zones of an estuary via laboratory leaching simulation experiment. The results indicated that seawater promoted a higher release of Cd and Cu than river water. However, the salinity induced by seawater did not significantly enhance the mobility of Pb. This implied that the mobility of Cd and Cu

can be reduced by the insufficiency of the salinity. The concentration of heavy metals in several sites, assessed in water, soil, and sediment samples, affected by different pollution sources are reported (Vareda et al., 2019). Although wastewater irrigation reduces the pressure on freshwater usage, it also leads to the accumulation of heavy metals in the soils. As reported by Mousavi et al. (2018), environmental risks based on metal mobility in greenhouses and fields in Baiyin City, Gansu, China had been irrigated with treated industrial and municipal wastewater. Results revealed that more than half of each studied heavy metal (72.6%−97.4%) was present in the residual fraction (F4), which is nonbioavailable. In addition, more information on the effects of HMs mobility in crop production is summarized (Dragicevic et al., 2018).

4.5 HEALTH AND ENVIRONMENTAL EFFECTS OF HEAVY METALS ON THE SOIL

The health and environmental effects caused by these heavy metals to human and aquatic life are enormous depending on their bioavailability and mobility. Šömen Joksić and Katz (2015) reported that heavy metals are primarily toxic, and the carcinogenic effects occurs when the water containing heavy metals is consumed. Although the attention has been shifted to effluent treatment lately, the presence of these metals in the river, dam, and underground water is the indication for further studies. The mobility of these metals from mining or other industries to the environment is the main cause of this problem. As such, heavy metals are low molecular weight elements that at certain concentrations can cause environmental problems as they accumulate. These metals can be toxic depending on their concentration despite being essential to the metabolism of most organisms. This section critically analyzed some of the health and environmental effects of these HMs on humans, animals, and the entire environment. The distribution of HMs such as Cu, Pb, Zn, and Cd in the particulate organic matter (POM) fractions at a zinc smelting waste slag site under in situ-aided phytostabilization after 5 years was studied. It was reported that POM significantly affects the distribution of heavy metals in contaminated soil. However, the effect of POM on the fate of heavy metals during in situ-aided phytostabilization of waste slag is unclear.

4.5.1 Health effects

The existence of HMs in human and animal bodies might be through the consumption of meat or food that may contain a variety of

contaminants, including heavy metals. The investigation on five heavy metals of serious concern (cadmium, lead, arsenic, chromium, and mercury) in meat products collected from major production provinces in China during 2015−17 were analyzed by multidimensional visualization and hierarchical cluster analysis. Meanwhile, the parameter estimation of the samples showed that the contents of the five heavy metals in other meat products (meat products except for cooked and premade meat products) were lower than those in cooked and premade meat products. Chromium was the highest in cooked and premade meat products when compared to other heavy metals (Wang et al., 2019). Furthermore, heavy metals in leachate during food waste composting may produce different degrees of pollution hazards and further induce environment costs, when the concentrations of heavy metals exceed the discharging quality standards. The quantitative evaluation of heavy metals' pollution health hazards was also reported by some researchers (Chu et al., 2019). It was found that the pollution hazard rate of *Cd* amounts to 94.03%, probably because *Cd*-containing materials such as plastics are mixed with food waste; therefore, the comprehensive pollution hazards rate is estimated as 94.48%. Another study discussed the effect of exposure to heavy metals in pregnant women in Beijing, China. The association of these heavy metals with birth weight and length of newborns was thoroughly analyzed (Xavier et al., 2019). Ten different HMs were measured including lead (Giles and Campbell, 2003), titanium (Ti), manganese (Momba et al., 2009), nickel (Ni), cadmium (Cd), chromium (Cr), antimony (Sb), stannum (Sn), vanadium (V), and arsenic (As), in 156 maternal and cord blood pairs. It was reported that Pb, As, Ti, Mn, and Sb showed high detection rates ($>50\%$) in both maternal and cord blood. Fourteen (9%) mothers had blood Pb levels greater than the United States Center for Disease Control allowable threshold limit for children ($50\,\mu\mathrm{g\,L}^{-1}$). In prenatal exposure to these heavy metals, there was no significant association between any heavy metal and birth weight/length (Li et al., 2019a). It was discovered that the contamination that started from highway toll station workers exposed to vehicle emissions during their working time could induce excessive reactive oxygen species generation and lead to significant health effects. Health assessment was conducted using integrated toxicity values and Monte Carlo simulation, and the results indicated that exposure to $PM_{2.5}$-bound heavy metals can trigger significant adverse. However, a comprehensive exposure investigation of environmental pollutants and oxidative stress levels must be conducted (Li et al., 2019b).

4.5.2 **Environmental effects**

4.5.2.1 ***Effects of heavy metals mobility on agricultural practices***

The availability of heavy metals in organic materials and in soil amended with these materials is of practical significance. They are used in the assessment of the purity of the soil environment and of the biological value of plants intended for human and animal consumption. Heavy metals such as Cu, Cd, Pb, and Zn in composts are investigated in sandy soil after the addition of composts such as sewage sludge and biochar. It was reported that the amount of Cd and Cu extracted with water in composts produced from maize straw was higher than the one determined in compost produced from maize straw. The content of Pb and Zn extracted with water in compost produced from maize straw, sewage sludge, and biochar was lower than in compost produced from maize straw (Mousavi et al., 2018). However, research reported some bacteria strains that can tolerate and consume heavy metals from the soil, which includes *Alcaligenes faecalis* MG257493.1, *Bacillus cereus* MG257494.1, and *A. faecalis* MG966440.1. These bacteria strains have been used as antioxidant agents and plant growth promoters under laboratory conditions. Their abilities were estimated in the presence of four heavy metals: zinc (Zn^{2+}) cadmium (Cd^{2+}), copper (Cu^{2+}), and lead (Pb^{2+}) at 1000 and 1500 mg L^{-1}. It was revealed that all tested strains were able to produce all estimated plant growth promoters in the presence or absence of heavy metals, and the highest amounts of all compounds were recorded in media free of heavy metals and decreased with the increase of heavy metals concentration. Furthermore, results proved that the three evaluated strains were considered as heavy metal tolerant-plant growth-promoting bacteria and have beneficial characteristics for remediating the contaminated mine tailing soil (Abou-Aly et al., 2019).

4.5.2.2 ***Effects of heavy metal mobility on aquatic and terrestrial animals***

Emerging aquatic insects are the main route of HMs transfer from aquatic-to-terrestrial food webs. The relative influence of these contaminants on animals and fishes resides in sea, rivers, and dams is enormous. It has been reported that one of the land use nearshore vegetation structure in Ohio, USA is contaminated with flux via the emergent aquatic insect subsidy on selenium (Se) and mercury (Hg) body burdens of riparian ants (Formica subsericea) and spiders of the family Tetragnathidae

along 11 river reaches spanning an urban-rural land-use gradient. Results indicated that fine-scale land cover in the riparian zone was positively associated with reach-wide body burdens of Se and Hg in both riparian *F. subsericea* and Tetragnathidae spiders. It was concluded that the improvement of the pathways and influences that control aquatic-to-terrestrial contaminant transport will be critical for effective risk management and remediation (Alberts and Sullivan, 2016). Terrestrial environmental inputs into freshwater ecosystems are very important. Resource fluxes (subsidy) from aquatic-to-terrestrial systems have been less studied, although they are of high ecological relevance, particularly for the receiving ecosystem. Results revealed a continuously increasing interest in the coupling of aquatic-to-terrestrial ecosystems between 1990 and 2014 (total: 661 studies), while the research domains focusing on abiotic (502 studies) and biotic (159 studies) processes are strongly separated. Approximately 35% (abiotic) and 25% (biotic) of the studies focused on the propagation of anthropogenic alterations from the aquatic to the terrestrial system (Schulz et al., 2015)

The trace metal accumulation and transfer within invertebrate food chains that are essential to envisage the ecological consequences of contamination, especially the behavior of trace metals in invertebrate food chains, were also investigated. The work found that essential trace metals had a far greater tendency to bioaccumulate in invertebrates than nonessential metals, but Cd was an exception. Reports demonstrate that accumulation can have no effect on some species and may actually prove beneficial to a few species at certain levels of exposure by increasing resistance to pesticides and immune response. In most invertebrates, negative effects on metabolism, fecundity, growth, developmental stability, and survival occur once accumulation exceeds a critical level. It was also reported that predators may be more vulnerable to trace metals than their prey, but there are greatly varying physiological differences among invertebrate species in all trophic levels that affect accumulation and detoxification of metals (Dar et al., 2019). The study of particulate plastics in the terrestrial and aquatic environments, such as small plastic fragments or beads (5 mm down to the nanometer range), was also conducted. They have been frequently referred to as "microplastics" or "nanoplastics." Research has identified particulate plastics as a vector for toxic trace elements in the environment. Thus these plastics can have severe environmental consequences, such as the development of metal toxicity, within aquatic and terrestrial organisms. Humans could also become exposed to particulate plastics through food chain contamination and airborne ingestion (Bradney et al., 2019).

4.5.2.3 **Effects of heavy metal mobility on surface water**

Heavy metals originated majorly from mining operations and other industries in which their usage is paramount. Mining operations, unlike other sectors, are fully reliant on the location of minerals with limited options to mitigate and adapt to regional water or quality impacts (Akinwekomi et al., 2016). Therefore, the greatest threat posed to water resources arises from mine discharges that have been found to be contaminated with heavy metals. The presence of some heavy metals in mine effluent is inevitable such as but not limited to iron and sulfate. Other common metals that can be found in mine effluents are Cd, V, Cu, Al, Cr, Hg, Pb, Zn, and Ni. An increase in industrialization and urbanization has constantly increased the demand for these metals, as they are mostly base materials in some productions. Some of them are used for pharmaceutical purposes, steel manufacturers, petroleum industry, electron acceptors, and additives to improve goods production. As the mining and usage of these metals increases, more risk is being posed to the environment. As such, the health and environmental effects caused by these heavy metals to human and aquatic life are enormous depending on their bioavailability.

The bioavailability, mobility, and origin of heavy metals present in sediments from the Anzali Wetland were investigated. These HMs (Cr, Co, and V) were identified and found that their origin was from another terrestrial environment via mobility. The metal As was mostly found in the reducible fraction (F3), whereas other metals were highest in the residual phase. The levels of Co present in the oxidizable fraction (F4); Pb and Cd present in the carbonate fraction (F2); and the other metals present in the exchangeable fraction (F1) were found to be the lowest. It was also reported in this study that Co and Pb have low risk at all stations due to lower accumulated concentration almost in all stations. However, enrichment factor analysis was found moderately enriched and other metals had a deficiency to minimal enrichment at all the stations (Bastami et al., 2018). Although the higher the concentration the vital the effects of most of these HMs on humans and the environment will be, some of these metals can be extremely dangerous even at trace levels. Climate change can also affect the mobility of heavy metals stored in soils and wetlands that can be released into the surface water upon bioavailability. This thus requires further review as it is discussed extensively in this chapter.

4.6 INEVITABILITY OF CLIMATE CHANGE

Climate change is a global problem that involves changes in temperature, precipitation, and weather condition. It is a change in climate that is

attributed directly and indirectly to human activity that alters the composition of the global atmosphere; therefore, natural climate variability was observed over a period of considerable time to evaluate its effect on soil mobility (Karmakar et al., 2016). Climate change is a problem that must be managed rather than solved. This is because there is overwhelming evidence that the climate is changing (Berrang-Ford et al., 2011) and could be managed before it results in any disaster. Many researchers have discovered before the climate change that global warming may extend beyond the dreaded 2°C and reach 4°C by 2100 (Henderson et al., 2015; Parry et al., 2009; Adger and Barnett, 2009). The major contributor to climate change is the greenhouse gas emission that is expected to increase due to increased industrial activities and technology development (Rose and Mccarl, 2008). The current climate changes are due to factors ranging from the consumption of nonrenewable resources to emission and subsequent accumulation of greenhouse gases (Hale, 2011). Climate change affects everything in the world such as agriculture and farming, human health, and water quality. For instance, farmers could experience enhanced crop growth because of increased atmospheric carbon dioxide, longer growing season, increased rainfall, and increased frequency of droughts, crop, livestock, and pests heat stress (Rose and Mccarl, 2008) as the climate changes. Soil quality is affected by geographical and climatic constraints (Doran and Parkin, 1994). Although agriculture has many benefits, it is vulnerable to disasters that include climate disturbances. Some agricultural activities are also known to contribute to climate changes, and these include the release of nitrous oxide from fertilized fields (Foley et al., 2011). Water availability is affected by the twin challenges of climate change and a growing world population. Population growth will increase water demand while climate change in arid and semiarid areas may reduce water availability (Grafton et al., 2014). Climate change is seen as a threat to the survival of species and the natural system's health (Erwin, 2009). Mobility is the term used in soil science to estimate the risk of contamination of other environmental compartments such as but not limited to heavy metals (Doumergue and Vedy, 1992). Excessive build-up of heavy metals in soils may contribute to environmental contamination especially in crop production, and consequently have an adverse effect on human health (Kananke et al., 2015). In this section, the effect of climatic change on the mobility of heavy metals shall be critically examined. The bioavailability of heavy metals in environmental and agricultural as contaminants in the soil is also critically discussed. Kim et al. (2015) defined the bioavailability of heavy metals in terms of plant uptake (phytoavailability) to describe both the concept and operation of bioavailability. It was explained that variation

of heavy metals solubility and mobility in soils depend on three factors that include specific and nonspecific adsorption, complex formation, and organic ligand affinity.

4.6.1 **Effects of climate change in the mobility of heavy metals**

One of the major issues facing the world today is the risk of large-scale climate change. The scientific community has agreed that the earth is getting warmer because of greenhouse gas emission, and if this should continue the consequence will be severe (Henderson et al., 2015). The industrial revolution came with many issues that include the continuous exposure of the earth ecosystem to a variety of potentially hazardous elements. These elements include cadmium, chromium, copper, nickel, zinc, and lead that have been found extensively in soil ecosystems and are nondegradable inorganic contaminants (Kim et al., 2015; Desaules, 2012). All these elements are classified as hazardous according to the United Nations Global Monitoring program although copper, nickel, and zinc are essential nutrients for humans and plants at low concentrations (Kaninga et al., 2019). Heavy metals contaminants are very common especially in the environment with high anthropogenic activities (Prudent et al., 2014; Wuana and Okieimen, 2011). These activities include industrial discharges, urban waste, disposal of high metal wastes, agriculture and animal wastes, use of phosphate fertilizers, coal combustion residue, spillage of petrochemicals, use of pesticides, and irrigation with wastewaters (Mousavi et al., 2013; Iqbal et al., 2011; Ahmad and Goni, 2010; Khan et al., 2008). One of the major routes that human is exposed to heavy metals is through the consumption of crops developed in highly contaminated soil (Kaninga et al., 2019). As such, soils and sediments have the capacity to store and immobilize chemicals until there is a change in the factors that influence storage capacity of soils and sediments, leading to change in the bioavailability of the stored chemical and consequently mobilization of the chemical into the environment (Stigliani et al., 1991). One of the major factors is climate change; there is a high potential for mobilization of heavy metals during an era of strong climatic change (Carlsson et al., 2017). This is because the capacity of soils to adsorb and immobilize heavy metals is strongly influenced by certain prevailing properties (Zhang et al., 2014). These properties include pH, redox potential, salinity, and organic content that directly affect the cation exchange capacity and soil structure (Diacono and Montemurro, 2015; Wang et al., 2014). Soil pH is one of the most important parameters that affect the mobility of heavy metals in the soil. The amount of hydrolyzed metals

increases with an increase in pH, and hydrolyzed metals are known to favor sorption reaction than free metals (Cappuyns and Swennen, 2008). The different metal complexes that are formed at different pH levels can differ considerably in their chemical characteristics, including solubility and toxicity. For instance, under alkaline conditions, metals can precipitate as hydroxides, oxides, phosphates, and carbonates, which could reduce their bioavailability. The redox potential is regulated by oxygen availability and has a significant influence on the mobility of heavy metals. Factors that determine soil oxygen availability include soil moisture conditions, microbial activity, and chemical oxygen demand. The oxidative condition of metals determines their solubility, uptake kinetics, and ability to form complexes. Salinity has a direct physical effect on soil structure due to high concentrations of sodium so that the cation exchange capacity of soil irrigated with saline water becomes populated with sodium creating sodic soil (Murray and Grant, 2007). Furthermore, organic contents in the soil serve as ligands donating electrons that are readily accepted by metals forming organometallic complexes. The presence of organics such as phenolic, humic, and fulvic acids in the soil can mobilize metals from soil to form stabile and water-soluble organometallic complexes (Tang et al., 2014; Rahman and Alam, 2010). Organometallics complexes form an important vector by which metals can be leached from soils and transferred to the ground- and surface water (Chen et al., 2010). The presence of organic matter may reduce the effects of heavy metal toxicity, even at high metal concentrations because organic ligands compete for heavy metal with binding sites on organisms (Violante et al., 2010; Olaniran et al., 2013).

However, these aforementioned properties are strongly affected by a climatic change either positively or negatively. Climatic change causes a change in temperature and rainfall leading to both annual and seasonal hydrological imbalances and thus affecting the soil moisture contents (Karmakar et al., 2016). The soil temperature and moisture affect the kinetics of microbial processes that determine the organic content of soils (Karmakar et al., 2016; Van Dijk et al., 2009; Stigliani et al., 1991). The effect of increasing soil temperature is to increase microbial decomposition leading to a decrease in the organic content of the soil. However, increasing soil moisture has the effect of increasing the organic matter content. Changes in the organic matter content of soils affect the mobility of heavy metals in two ways (Stigliani et al., 1991). First, decreases in organic matter cause an increase in the erosion of soils. Because pollutants tend to accumulate in the upper part of the soil, the flux of metals from soils to the aquatic environment increases. Extreme climatic events,

which could be more frequent in the future, could cause an even greater rate of erosion. Second, the cation exchange capacity of the soil is directly proportional to its organic matter content. A decrease in organic matter content leads to reduced cation exchange capacity resulting in a lower capacity of the soil to adsorb heavy metals.

Soil moisture directly affects the redox potential (Husson, 2013). Wet and waterlogged soils rich in organic matter, which are found in peat regions and wetlands, typically have low levels of dissolved oxygen and thus low redox levels (Schulz et al., 2015). Dry soils, particularly if they are porous and well aerated, tend to have higher redox potentials. Thus drying out of wetland areas could cause extensive changes in redox potential, which could affect the mobility of any heavy metals stored there as insoluble sulfides. Under dry conditions, these metals may be mobilized as soluble sulfates. Soil moisture is indirectly linked to salinization (Ondrasek et al., 2011). If soils dry out in summer in agricultural regions, farmers may increase their reliance on irrigation to maintain crop productivity. When the rate of evapotranspiration is greater than the rate of precipitation, soils irrigated with water from areas where the groundwater is highly saline become increasingly saline (Flores et al., 2016; Liu et al., 2019). Soils with increased salinity have a decreased capacity to store heavy metals leading to an increase in heavy metal mobility (Acosta et al., 2011). This means that the capacities of soils to store heavy metals could be significantly reduced under warmer, drier conditions (Wilson and Bell, 1996; Acosta et al., 2011), and this could be confirmed by their bioavailability.

4.6.2 Bioavailability of heavy metals with weather pattern in South Africa

The form in which heavy metals are present is determined by their mobility and bioavailability in the soil environments (Violante et al., 2010). Heavy metals can occur in the environment as in both soluble and particulate forms (Tomás et al., 2012). Weather patterns can affect the form in which heavy metals occur in the environment (Jeričević et al., 2012; Van Dijk et al., 2009; Wijngaard et al., 2017). In South Africa due to mining and other anthropological activities, some heavy metals that include Pb, Zn, V, Bi, Ni, Li, As, Sn, Co, Cu, Mo, Sb, Hg, and Se have been found in the environment (Mtunzi et al., 2015; Durand, 2012; Kootbodien et al., 2012; Olobatoke and Mathuthu, 2016). As such, the higher distribution of zinc, cadmium, copper, iron, manganese, and lead was found in seawater and in sediment samples obtained from the East London and Port Elizabeth (Fatoki and Mathabatha, 2001).

Mtunzi et al. (2015) also reported that the concentration of lead (Pb) is above the allowable discharge limit at the farm and the township of a certain part of Johannesburg. Residents in the West and Central Rand, an area encompassing Johannesburg and its surroundings, have been found to be exposed to elevated concentrations of heavy metals and radiation that can contribute to immediate and long-term medical problems such as asthma, skin rashes, cancer, and organ damage. Furthermore, heavy metals contamination of the soil samples obtained from the Rustenburg mining area was found to be relatively high and dominated by nickel and chromium (Gzik et al., 2003). Okonkwo and Mothiba (2005) reported cadmium and lead contamination in three different rivers (Dzindi, Madanzhe, and Mvudi) of Thohoyandou, Limpopo Province. Mercury emissions have also been found to be very high in South Africa because of coal combustion and gold mining (Fayiga et al., 2018).

4.6.3 Assessment of heavy metals type based on weather pattern

Heavy metals get through the atmosphere and water through dispersion and deposition processes leading to the accumulation in soils and water sediments. This consequently becomes reservoirs for other seminatural releases of heavy metals back to the atmosphere and other media. Both the strength and spatial patterns of heavy metals release naturally depend on climate conditions and change accordingly. Whenever there is a rise in temperature, the soil water content decreases as evapotranspiration increases, leading to the higher resuspension of soil dust particles. Jeričević et al. (2012) suggested that the best response to these contamination conditions would be site-specific in view of impending climate change conditions. This can be determined by perceived contamination pathways that would be influenced by the end-use purposes for the sites in the nearest future. This is due to the fact that there are complex interactions between climate parameters and soil properties. Weather conditions, such as wind speed and direction, temperature, and humidity, can also influence the concentrations of particulate matters that serve as carriers of heavy metals (Suvarapu and Baek, 2017). According to Hailin et al. (2008), concentrations of particulate matters were higher during the winter period in the year 2001 up to 2004 and became very low between the years 2005 and 2006. Ambade (2014) also reported a higher concentration of heavy metals in the winter than in the summer. This was attributed to strong solar radiation in summer and the presence of secondary aerosols in the air. The wind direction has been observed to play a major role in the concentrations of heavy metals present in particulate matter.

For example, Tan et al. (2014) reported more than 20 times higher concentration of Cd in the northwest wind direction than in the other wind directions at Sansui district, China. This was as a result of transport from the aluminum industries that are located near the site where the sampling took place. Lee and Park (2010) observed that the concentrations of heavy metals in ambient air at the industrial city of South Korea during misty days were significantly higher than on clear days. Lee and his coworkers attributed this observation to the differences between the meteorological conditions, such as relative humidity and ambient ventilation indices during misty days and clear days. Pekey et al. (2010) found higher ambient concentrations of Al, Si, Ca, Ti, Mn, and Fe in summer, while V, Ni, Cu, Zn, As, and Pb were higher in winter. This was due to the easy suspension of crustal elements (Al, Si, Ca, Ti, Mn, and Fe) in summer due to the dryness of soils. The concentrations of V, Ni, Cu, Zn, As, and Pb, were higher during the winter period, which related to the increasing industrial production, high atmospheric stability, and strong low-level morning temperature inversions causing low mixing height conditions in winter. Alleman et al. (2010) reported that the wind direction had no influence on the concentrations of particulate matter measured at a French industrial zone but a favorable wind direction tends to disperse the sources of particulate matter over the sea. Stortini et al. (2009) observed higher particulate matter because of high humidity; however, frequent rain and high wind speeds caused a decrease in the level of particulate matter observed at the lagoon area in Venice.

4.7 EXISTING TECHNOLOGIES TO MINIMIZE HEAVY METALS MOBILITY, BIOAVAILABILITY IN SOIL AND WATER, AND THEIR LIMITATIONS

4.7.1 Existing water treatment technologies for the removal of heavy metals

The mobility of heavy metals in surface water starts either from underground or from industrial discharges. However, there are different technologies used for the removal of heavy metals from surface water but their applications depend on the basis for the treatment. For instance, techniques used efficiently for the removal of the anion (sulfate) might not be suitable for the total removal of other metals from surface water or for the polishing of industrial effluent. One of the major conventional and highly efficient techniques for heavy metals removal is chemical precipitation whereas little or no achievement has been recorded for precipitation of dyes.

Chemical precipitation processes involve the addition of chemical reagents, followed by the separation of the precipitated solids from the cleaned water. Amaral Filho et al. (2016) reported the use of this technology in sulfate-bearing AMD (coal and metal sulfide) and the separation was done via floatation. The result revealed that the maximum removal percentage (80%−82% of the feed content) appears to be limited by the efficiency of the dissolved air flotation process and the chemical equilibrium of the precipitates, which leave some soluble sulfate in the solution. The limitation of this technique is basically the formation of alkaline sludge, therefore, it usually requires a large settling tank, therefore further treatment might be needed. The use of biosorbent such as cellulosic material has reduced the formation of alkaline sludge and also eco-friendly. For instance, Riordan et al. (1997) combined precipitation and biosorption methods using residual brewer's yeast as biosorbent media and reported 360 mg g^{-1} biosorption capacity, and this confirms the efficiency of these methods but highly environmentally friendly material must be applied. Coagulation/flocculation is also more of a physical technology used for the removal of bigger or smaller particles from wastewater before undergoing any chemical treatment. This method is also highly efficient for the removal of heavy metals especially when it involves very low concentration (Amuda et al., 2006).

Advanced oxidation that includes photocatalysis degradation has been proven highly efficient in heavy metals (Cr) removal. The ability of the technique is to completely mineralize the target pollutants, without forming any residual sludge. Photocatalysis is a photo-induced reaction that is accelerated by the presence of a catalyst. In this reaction, activation is brought about by the absorption of a photon with energy that is equal to or higher than the bandgap energy of the catalyst. The promotion of an electron from the valence band semiconductor catalyst to the conduction band leads to charge separation which then causes the generation of an electron−hole pair in the valance band; therefore, the choice of catalyst is significant for degradation of chromium. Yinmao et al. (2014) investigated the enhanced photocatalytic degradation of dyes and heavy metals using graphene/Pd/TiO$_2$ nanocomposites. Comparison of photocatalytic degradation of rhodamine B by TiO$_2$-NWs, Gr/Pd/TiO$_2$-NPs, and Gr/Pd/TiO$_2$-NWs nanocomposites was investigated under ultraviolet light irradiation. The results confirmed that the Gr/Pd/TiO$_2$-NWs composite revealed higher photocatalytic activity based on the higher surface area of the TiO$_2$ substrate in the nanowire structure.

Adsorption/desorption and ion-exchange water treatment techniques can efficiently remove heavy metals from industrial effluent but their

drawbacks can also not be overlooked. Resins are the major ion-exchange media depending on the chemistry of water to be treated. The anion resin, for example, targets the vanadium in the water while the cation removes nickel. Once exhausted, vessels are returned to the processing facility where the contaminants are removed from the media/resin. This process is environmentally friendly, and not too expensive to maintain. Anion and cation resins, as well as ion-exchange membranes, are the common ion-exchange media in wastewater treatment. Adsorption is mainly a surface process, which occurs when a gas or liquid solute gathered on the surface of adsorbent media, forming a molecular or atomic film. Adsorption can be applied for different purposes but quite robust in terms of wastewater treatment efficiency. It is highly economical, but mostly depending on the choice or type of adsorbent used. Adsorbents are usually in the form of moldings, spherical pellets, or rods. Adsorbent must possess high abrasion resistance, to enhance surface capacity for adsorption as a result of higher exposed surface area. They should also possess a distinctive pore structure and diameter that allows the fast transportation of the vapors. This process can be used for the treatment of metals and dye-containing effluent. As mentioned earlier, the performance of any of these existing technologies depends on the choice of suitable media.

To mitigate the serious ecological problems and risks to human health that are posed by heavy metals in the soil, it is important to enhance the efficiency of heavy metal extraction by washing contaminated soil using chemical methods. Secondary pollution of soil by chemical chelating agents has, however, brought a new threat to the environment. Here, we describe a biodegradable lignin-based poly(acrylic acid) (LBPAA) composite that was designed as a chelating agent to wash soil contaminated with Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions. Extraction and ion transfer of heavy metal ions by the LBPAA composite improved the remediation rate of contaminated soil during water leaching. After washing five times, the LBPAA-assisted elution process reduced the amount of Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions in contaminated soil to 22.57%, 52.60%, 13.63%, and 17.95%, respectively. These values are 2.39-fold, 5.04-fold, 5.04-fold, and 1.31-fold, respectively, better than elution with deionized water. Additionally, LBPAA is able to sequester Cd^{2+} and Pb^{2+} ions from the contaminated soil and transfer them to the eluent. In summary, this work provides a safe, environmentally friendly and sustainable remediation strategy for heavy metal-contaminated soil. Specifically, the changes in heavy metal mobility and availability in contaminated wetland soil remediated using lignin-based poly(acrylic acid) was demonstrated in the field of soil remediation (Zhao et al., 2019)

4.7.2 **Existing technologies to minimize heavy metals mobility, bioavailability, and their limitations in soil**

The remediation of heavy metals requires special attention to protect soil quality, air quality, water quality, human health, animal health, and all spheres as a collection (Masindi and Muedi, 2018). There are existing or developed physical and chemical heavy metal remediation technologies that include adsorption (sorption/desorption), solution complexation, oxidation—reduction, precipitation—dissolution reactions surface capping, sequential extraction encapsulation, landfilling, soil washing, solidification, and vitrification. These techniques have been proven to be highly efficient in identifying and minimizing heavy metals in the soil; however, their limitations that include operational costs, time consuming, and release additional waste to the environment cannot be overlooked (Liu et al., 2018). Recently, phytoremediation, electrokinetic extraction, and chemical stabilization remediation strategies that include physical and chemical methods (abiotic) or biological activities have been shown to impede the migration of radionuclide and metal contaminants within soil and groundwater. However, abiotic remediation methods are often too costly owing to the quantities and volumes of soils and/or groundwater requiring treatment.

Surface capping is a method whereby the contaminated site is covered with a layer of waterproof material to form a stable, protection surface. The method does not actually remove or reduce the heavy metal contaminants but eliminates the risk of incidental ingestion and skin contact. The method is simple, rapid, and effective but it is applicable to small but highly contaminated areas. The cap on the surface of the area makes it impermeable to water so that further contaminations due to diffusion by both surface and underground water can be prevented.

Encapsulation also termed liner, barrier, or cutoff wall technique is similar to surface capping and sometimes used as an alternative to surface capping. This technique involves the isolation of the contaminated field and the enclosure of the pollutants. The purpose is to eliminate the off-site dispersion of the contaminants and on-site bio-exposure to the contaminants (Meuser, 2012), Synthetic textile sheets or clay layers are used as low permeability caps to minimize surface water contact and consequently prevent leaching of contaminants into the groundwater. The technique is used when the site is of a small area, shallow, and is seriously contaminated. It is an alternative treatment method commonly used to manage sites that are contaminated by radionuclides, asbestos, PAHs,

heavy petroleum hydrocarbons, and mixed wastes. The main challenge of encapsulation is the construction of underground vertical impermeable walls at contamination sites. Commonly used walls are slurry walls, thin walls, sheet pile walls, and injection walls (Bradl, 2005).

Soil flushing involves the removal of contaminants from the soil in situ by passing an extraction fluid through the soil. At the end of the process, the extraction fluid is recovered, reused, and eventually treated and disposed. The technique is applicable to homogenous, coarse-textured soils with high permeability (Liu et al., 2018). The extraction fluid must be designed for specific characteristics to effectively extract heavy metals from the soil. Although citric acid and tartaric acid have been tried, EDTA has been found to be the most efficient extraction fluid relative to water, surfactants, and cyclodextrin, flushing out 25%−75% of the Cu, Zn, and Pb in industry-contaminated loam sand (pH 7.0, OM 11.1%) columns (Liu et al., 2018).

Chemical immobilization is an in situ technique also known as in situ solidification/stabilization. It is a technique used to trap or immobilize pollutants in the contaminated soil by introducing chemical agents into the original medium to solidify the soil or convert the mobile pollutant fractions into precipitates and/or strongly sorbed moiety. Chemical immobilization only demobilizes the metals and does not remove them. Chemical immobilization is used to reduce the mobility and solubility of heavy metals and their concentrations in the soil pore water. This leads to the reduction of the potentials of transport to plants, microorganisms, and water (Tajudin et al., 2016).

Ex situ solidification is another well established, timely efficient technique but relatively expensive soil remediation technology that has been implemented in soil remediation projects. The technique involves the removal of metal-contaminated soil from the site, transportation to treatment facility, screening to exclude coarse materials, and mixing with a binding substance in an extruder. The technology is also called microencapsulation because the contaminants are encased in a waterproof solid entity formed by the dispersion of the binding substance through the soil. The binding materials that are currently used for contaminant encapsulation include molten bitumen, modified sulfur cement polyethylene, emulsified asphalt, pozzolan cement, and portland cement. The technique is called ex situ stabilization if a stabilizing agent is used instead of a binding substance to immobilize contaminants through chemical reactions (Liu et al., 2018).

Landfilling, also known as "dig and haul," is the simplest soil remediation and well-established method for cleaning up hazardous waste sites.

The method involves the removal of the contaminated soil from its original site and its transportation to a well-secured landfill for disposal. A secure landfill is an engineered structure with impermeable liners, leachate drains, and dike enclosures. The double liners (a plastic layer and a clay layer) and the leachate collection and monitoring system are integral components of the facility to prevent potential leakage and groundwater contamination. The top cap/liner system is to minimize rainfall infiltration and keeps surface runoff away from the fill. Design, construction, and use of a secure landfill are subject to governmental laws and regulations.

Soil washing is a combination of physical and chemical processes to remove heavy metals from contaminated soil by first removing the soil and subsequent washing of the soil ex situ with specially formulated chemical solutions. The contaminated soil is excavated from the site, then crushed and screened to remove coarse materials such as plastic residues, woods, and stones. The magnetic materials are removed from the soil by the use of magnets. The screened soil is thoroughly mixed with a washing solution by sonication or mechanical agitation. The soil and washing solution are then sieved or hydrocycloned to separate coarse sand and gravels from the fine silt and clay fraction (0.05 mm). The coarse fraction is less contaminated and is typically returned to the original site after water rinsing. The silt and clay particles suspending in the washing solution are recovered by settling, rinsed with water, and returned to the original site. The waste washing solution and rinsing water are reused, recycled, or conveyed to a wastewater treatment facility for disposal. The wastewater treatment sludge is further treated by solidification/stabilization before landfilling. Soil washing relies on washing solutions to mobilize heavy metals by altering soil acidity, solution ionic strength, redox potential, or complexation. An ideal washing solution should dramatically improve the solubility and mobility of heavy metal contaminants yet interact weakly with soil constituents and should be nontoxic and biodegradable. Chemicals commonly used as washing solution include hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, fluorosilicic acid, formic acid, acetic acid, oxalic acid, citric acid, tartaric acid, polyglutamic acid, and EDTA. Overall, hydrochloric acid, EDTA, and subcritical water demonstrated the highest washing efficiency over a wide range of heavy metals and soils (Yang et al., 2018).

Vitrification is a proven and commercially available technology. This is a thermal remediation technique that uses heat to transform contaminated soil into glass-like solids. It a destructive technology involving the application of intensive energy to contaminated soil to form a

high-temperature zone (1500°C). Although highly effective, the soil cannot be used for agricultural purposes after a vitrification process. Usually, the soil in the zone is then melted into molten "lava" and becomes glass-like material upon cooling (Meuser, 2012). The heavy metals are encapsulated in the glassy matrix while any organic contaminants are destroyed. The resultant vitrification structure is strong, durable, chemically inert, and resistant to leaching. There are the main types of vitrification depending on the source of energy used for the process. Electrical vitrification involves the use of high voltage electricity that is imposed on graphite electrodes inserted in the contamination site at a predetermined spacing to generate heat. Thermal vitrification is a process whereby an external heat source such as microwave radiation or natural gas is used to heat a rotary retort containing contaminated soil. Plasma vitrification achieves high temperatures through electrical discharge-induced gas plasma (Tu et al., 2010). The technique can be applied both in situ and ex situ although it is commonly used as an in situ process.

4.8 NOVEL/CURRENT TECHNOLOGIES TO MINIMIZE HEAVY METALS MOBILITY REGARDLESS OF CLIMATIC CHANGE

Metal pollution has serious implications for human health and the environment. Therefore, remediation of heavy metals contaminated soil could be the only effective option to reduce the negative effects on ecosystem health (Mahar et al., 2016). Toxic metal pollution of waters and soils is a major environmental problem, and unfortunately, the current conventional remediation approaches do not provide acceptable solutions. This is because the current remediation methods of heavy metal from contaminated soil and water are expensive, time consuming, and environmentally destructive. Unlike organic compounds, metals cannot degrade, and therefore effective clean-up requires their immobilization to reduce or remove toxicity. In recent years, scientists and engineers have started to generate cost-effective technologies that include the use of microorganisms/biomass or live plants to clean polluted areas.

4.8.1 Bioremediation

Bioremediation is a natural process involving the use of microorganisms and/or plants for the treatment of polluted soils (Chibuike and Obiora, 2014). It is a cost-effective and nondisruptive method of soil remediation, but it is usually time consuming and at times affected by the climatic and geological conditions of the site to be remediated (Blaylock et al., 1997;

Schmöger et al., 2000). The mechanism of bioremediation involves the transformation of heavy metals from one organic complex or oxidation state to another. Due to a change in their oxidation state, heavy metals can be transformed to become either less toxic, easily volatilized, more water-soluble, less water-soluble, or less bioavailable because of a change in their oxidation state (Garbisu and Alkorta, 2003). It is noted that when heavy metals are more water-soluble, they can be easily removed by applying leaching. However, when they become less water-soluble, they precipitate and become easily removed from the environment. Bioremediation can be effectively used for the treatment of heavy metal-polluted soil. It is most appropriate when the remediated site is used for crop production because it is a nondisruptive method of soil remediation. Using plants for bioremediation (phytoremediation) is a more common approach to bioremediation of heavy metal compared with the use of microorganisms.

4.8.1.1 *Phytoremediation*

Phytoremediation is an emerging technology for cleaning up contaminated sites, which is cost-effective and has aesthetic advantages and long-term applicability. The technology involves the use of specially selected and engineered metal-accumulating plants to remove, detoxify, or immobilize environmental contaminants in a growth matrix (soil, water, or sediments) through the natural, biological, chemical, or physical activities or processes of the plants. It is best applied at sites with shallow contamination of organic, nutrient, or metal pollutants that are amenable to one of the five applications. The environmental clean-up is an emerging technology called phytoremediation. The content of this technology is applicable to toxic metal remediation that includes phytotransformation, rhizosphere bioremediation, phytostabilization, phytoextraction, and rhizofiltration (Conesa et al., 2012; Cunningham and Berti, 2000; Cunningham et al., 1995; Jadia and Fulekar, 2009)

Phytotransformation, which is also referred to as photodegradation, is the breakdown of organic contaminants sequestered by plants through metabolic processes within the plant or through the effect of compounds, such as enzymes, produced by the plant (Singh and Jain, 2003; Ghosh and Singh, 2005). Rhizosphere bioremediation: Rhizosphere bioremediation also known as rhizodegradation is the enhanced biodegradation of recalcitrant organic pollutants by root-associated bacteria and fungi under the influence of select plant species. Vegetation can increase the total number of beneficial fungi and bacteria in contaminated soil from a general rhizosphere effect (Olson et al., 2003). Phytostabilization is the use of plants to

eliminate the bioavailability of toxic metals in soils. Phytostabilization involves the establishment of a plant cover on the surface of the contaminated sites with the aim of reducing the mobility of contaminants within the vadose zone through accumulation by roots or immobilization within the rhizosphere, thereby reducing off-site contamination (Bolan et al., 2011). Phytoextraction is the use of metal-accumulating plants to remove toxic metals from soil. Phytoextraction is a subprocess of phytoremediation in which plants remove dangerous elements or compounds from soil or water, most usually heavy metals that have a high density and may be toxic to organisms even at relatively low concentrations (Barbosa et al., 2018; Conesa et al., 2012). The heavy metals that plants extract are toxic to the plants as well, and the plants used for phytoextraction are known hyperaccumulators that sequester extremely large amounts of heavy metals in their tissues (Ali et al., 2013). Plants intended for this application are called hyperaccumulators. These species of plants have a high tolerance to heavy metals and are capable of absorbing a larger amount of metal in comparison to other plants. Rhizofiltration is the use of plant roots to remove toxic metals from polluted waters (Dushenkov et al., 1995). Rhizofiltration is an important process going on in soil under various soil and environmental conditions. It corresponds to the accumulation of compounds from soil aqueous solutions by the adsorption on the surface of roots or assimilation through the roots and transmission to the aerial parts.

4.8.1.2 *Application of clay materials in soil remediation*

Typical clay minerals, natural sepiolite, palygorskite, and bentonite, have been widely utilized for the in situ immobilization of heavy metals in soils, especially Cd-polluted paddy soils and wastewater-irrigated farmland soils (Yi et al., 2017). Clay minerals are able to increase soil pH, decrease the chemical-extractable fractions and bioavailability of heavy metals in soils, and reduce the heavy metal contents in the edible parts of plants. The immobilization effects have been confirmed in field-scale demonstrations and pot trials. Clay minerals can improve the environmental quality of soils and alleviate the hazards of heavy metals to plants. As main factors affecting the immobilization effects, the pH and water condition of soils have drawn academic attention. The remediation mechanisms mainly include liming, precipitation, and sorption effects. However, the molecular mechanisms of microscopic immobilization are unclear. Future studies should focus on the long-term stability and improvement of clay minerals to obtain a better remediation effect. The advantages of using clay minerals include low cost, abundant reserves, and high performance (Yi et al., 2017).

Clay minerals used as amendments for heavy metal-polluted soils include sepiolite, palygorskite, and bentonite. The remediation effects of sepiolite, $Mg_8Si_{12}O_{30}(OH)_4(H_2O)_4 \cdot 8H_2O$, a porous fibrous hydrated magnesium silicate, have been confirmed in many field demonstrations and pot trials. The advantages of sepiolite have been shown in the remediation of Cd-polluted acid paddy soils on a field scale, including its high performance, universal applicability, low cost, and simplicity of use (Yin et al., 2017). Sepiolite alone or in combination with other materials such as limestone can significantly reduce the Cd content of brown rice, regardless of its use in pot trials or in field demonstrations (Yin et al., 2017; Cao et al., 2018). Palygorskite, $(Mg, Al)_2Si_4O_{10}(OH) \cdot 4(H_2O)$, also known as attapulgite, is a magnesium aluminum phyllosilicate and was found to have good sorption capacity to remove Cu, Zn, Cd, and nickel (Ni) from aqueous solutions (Murray et al., 2011; Sheikhhosseini et al., 2013). The challenges of using clay include differences in the chemical composition of sepiolite will lead to differences in the remediation effect determination of appropriate doses.

4.8.2 Electrokinetic extraction

Electrokinetic remediation is a method being developed to use electric current to remove heavy metals from contaminated soil. There are many demonstrations and pilot plants all over the world, but the method is yet to be commercialized (Hansen et al., 2016). Electrokinetic extraction is the method used to extract heavy metals from contaminated soils through electrical adsorption. It involves the application of low-density direct current (DC) electricity into the soil. The cations in the solution phase of the contaminated soil can also migrate to the cathode while anions migrate to the anode at the attractive force of the established electrical field. Consequently, the metal contaminants concentrated at the electrodes are removed by electroplating, (co-) precipitation, solution pumping, or ion-exchange resin complexation.

Electrokinetic remediation depends on the velocity at which the metal ions move through the soil and may take a few days to several years to complete. The mechanism of migration of the metal ions under the applied DC electric field is through electroosmosis, electromigration, electrophoresis, and diffusion. Electro osmosis is the movement of water from anode to cathode and can be applicable to nonionic species due to the electroosmosis-induced water flow. Electromigration involves the movement of ions to the counterpart electrode while electrophoresis is the movement of charged colloidal particles. The diffusion transport is also induced by the concentration gradients across the soil profile.

Among the factors that determine the direction and the quantity of heavy metal, migration includes the metal species, charge density, hydrated radius, metal concentration, chemistry of soil solution, soil moisture content, soil type, and the structure (Liu et al., 2018).

4.9 CURRENTLY DEVELOPED PROTOTYPE AND THEIR ACTIVITIES IN REDUCING THE MOBILITY OF HEAVY METALS

4.9.1 Asymmetrical alternating current electrochemistry

Xu et al. (2019) reported the design and demonstration of a remediation method based on a concept of asymmetrical alternating current electrochemistry. The technique combines a recirculating soil washing system with an electrochemical filtration. It was able to eliminate secondary pollution by recycling soil washing chemicals. The treatment transformed heavy metals and reduced them to zero-valent metallic states. The technique was able to remove different metals including copper, lead, and cadmium at different initial concentrations ranging from 100 to 10,000 ppm. Accepted regulation limits for each were achieved between 30 minutes and 6 hours of treatment without excessive nutrient loss from the treated soil and also without the production of secondary toxic products. They conducted a long-term experiment and plant assay, which revealed that the method is sustainable and feasible for use in agriculture.

The construction of an asymmetrical alternating current electrochemistry (AACE) remediation method is as shown in Fig. 4.1. The figure shows a recirculating chelating agent washing system and an AACE filtration device. The soil is excavated from contaminated sites and loaded into a treatment cylinder containing a solution of two EDTAs in reservoir tanks attached on each side. A water pump is used to circulate the EDTA solution to wash the contaminated soil thoroughly. The soil-sorbed heavy metal cations are mobilized by forming heavy metal−EDTA complex and transported to the AACE filter, which is connected to an alternating current power supply. Fig. 4.1B shows an illustration of the AACE filter, composed of two parallel amidoxime-functionalized porous carbon (Ami-PC) electrodes and a separator. After the AACE filtration, heavy metal cations are liberated from their chelation complex and electrodeposited to metallic states on the working electrode, and the EDTA solution is recycled for repeated use. The Ami-PC electrode was fabricated by coating a carbon felt with precursor slurry of polyacrylonitrile (PAN) and activated carbon, followed by a hydrothermal reaction to substitute the
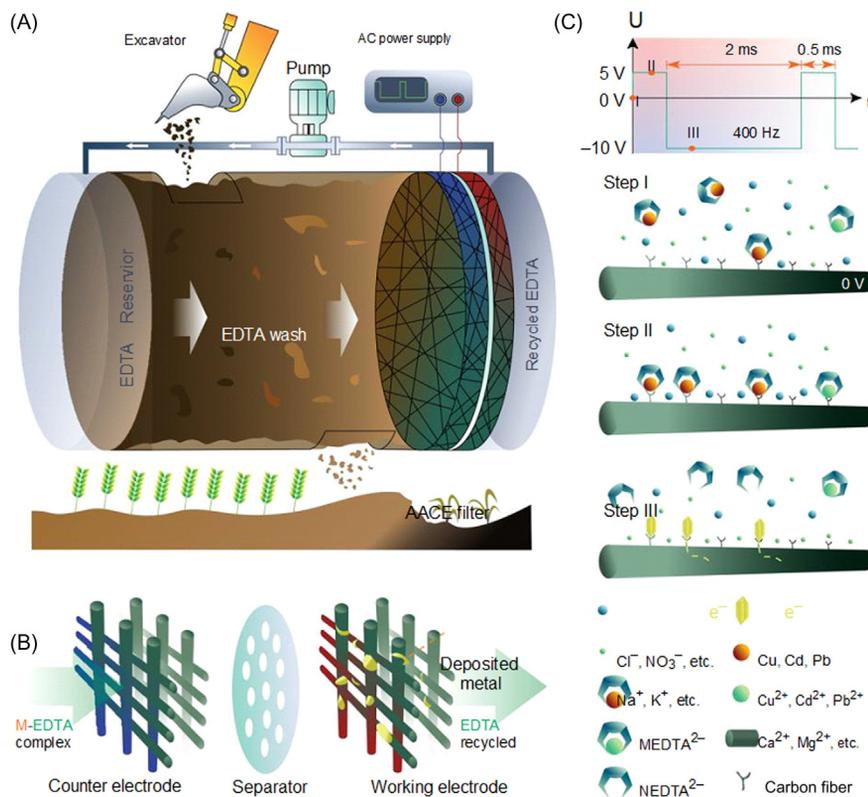
■ **FIGURE 4.1** Working principle of AACE (A. Schematic of an AACE remediation system. B. Illustration drawing of the AACE filter, composed of two parallel Ami-PC electrodes and a separator C. The waveform of the applied bias and the physical process in the AACE filtration) (Xu et al., 2019).

nitrile functional groups in PAN with amidoxime functional groups. The amidoxime has two functions: to modify the carbon felt surface to hydrophilic, the high surface area of the electrodes can be fully utilized. This also provides strong chelation sites that can compete with EDTA to bind heavy metal cations and hence promote the electrodeposition efficiency.

4.9.2 **Use of biochar**

Many researchers are currently investigating the use of biochar for remediation of soil contaminated by heavy metals. Puga et al. (2015) reported

their work where they used biochar to treat contaminated soil to reduce the availability and plant uptake of zinc, lead, and cadmium. The biochar was derived from sugar cane straw. The application of biochar (BC) decreased the available concentrations of Cd, Pb, and Zn in 56%, 50%, and 54% respectively, in the mine contaminated soil leading to a consistent reduction in the concentration of Zn in the pore water (first collect: $99-39$ mg L^{-1}, second: $97-57$ mg L^{-1}, and third: $71-12$ mg L^{-1}). The application of BC reduced the uptake of Cd, Pb, and Zn by plants with the jack bean translocating high proportions of metals (especially Cd) to shoots. This study indicated that biochar application during mine soil remediation reduced plant concentrations of potentially toxic metals. Lucchini et al. (2014) demonstrated that biochar made from wood did not increase the concentration of metals in soil and could be safely applied for agricultural purposes. Méndez et al. (2012) investigated the use of biochar obtained from the pyrolytic conversion of sewage sludge and concluded that it could be a sustainable option for the management of the Mediterranean. The risk of leaching of Cu, Ni, and Zn was found to be lower in the soil treated with biochar. Jiang et al. (2012) investigated the use of biochar obtained from rice straw to immobilize Cu(II), Pb(II), and Cd(II) in a simulated polluted Ultisol. They found that the heavy metal contents change a little by the addition of biochar. The incorporation of biochar made the negative soil surface charge more negative and increased the soil pH, and this was advantageous for heavy metal immobilization in the bulk soil. As the amount of biochar increased, the acid-soluble Cu(II) and Pb(II) decreased by $19.7\%-100.0\%$ and $18.8\%-77.0\%$, respectively. The descending range of acid-soluble Cd(II) was $5.6\%-14.1\%$, which was much lower than that of Cu(II) and Pb(II). When 5.0 mmol kg^{-1} of these heavy metals were added, the reducible Pb(II) for treatments containing 3% and 5% biochar was 2.0 and 3.0 times higher than that of samples without biochar, while the reducible Cu(II) increased by 61.6% and 132.6% for the corresponding treatments, respectively. When 3% and 5% biochar was added, the oxidizable portion of Pb(II) increased by 1.18 and 1.94 times, respectively, while the oxidizable portion of Cu(II) increased by 8.13 and 7.16 times respectively, primarily due to the high adsorption affinity of functional groups of biochar to Cu(II). Al-Wabel et al. (2015) showed from their word that biochar application to heavy metal-contaminated soil has the potential for heavy metal immobilization. They found that biochar addition. It was concluded that biochar can be used to enhance metal phytostabilization of contaminated soils as well as improved plant growth and some soil physical properties.

4.10 SUMMARY

The mobility and bioavailability of heavy metals in soil and water are the major sources of contaminants in food and surface water, especially, in developing countries. The health and environmental effects of heavy metals in soil and water as well as the factors affecting the mobility of heavy metals such as climatic change are thoroughly reviewed in this chapter. The outcome and limitation of existing treatment technologies in mining applications were also reviewed. The current and novel techniques used in minimizing the mobility of heavy metals such as but not limited to bioremediation, phytoremediation and AACE technologies for heavy metals remediation are also discussed. It is hereby concluded that long-term and outstanding research is also required to eradicate the mobility and bioavailability of heavy metals in soil and surface water to prevent their adverse effects on humans and the environment.

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