

Review Article

A Review on: Heavy metals pollution in soil and their remediation techniques

Abstract

Heavy metals are naturally occurring elements with large atomic weights and densities that are at least five times greater than those of water. Their widespread dispersion in the environment as a result of their numerous agricultural, industrial, residential, medicinal, and technical applications has raised questions about their possible consequences on human health as well as environment. A broad review of heavy metal clean-up technologies is included in this paper. The following technologies are described together with the destiny of heavy metals: Bioremediation, stabilization/solidification, separation, and concentration are examples of in-situ and ex-situ technologies. electrokinetics, Soil flushing, barriers and treatment walls, treatment by chemical, soil amendments, and phytoremediation are examples of in-situ technologies. One of the ex-situ processes is soil cleaning.

Key words: residential, environment, bioremediation, electrokinetics

Introduction

The health and manageable advancement of soil ecological system are firmly connected with human prosperity. In 2015, 13 of the 17 global sustainable development goals mentioned in "Transforming our world: The 2030 Agenda for Sustainable Development."

Released by the UN has anything to do with soil, either directly or indirectly. However, with the quick advancement of contemporary civilization, the unquestionably challenging problem of soil contamination has evolved into one of the most important threats to food safety and public health, arousing unavoidable public concern.

The heavy metals (HMs) in side of the road soils and grass of expressways look for worldwide consideration because of expansion in rush hour gridlock loads (Adeniyi and Owoade 2010; Bernardino et al. 2019). Be that as it may, the level of HMs in the side of the road soil may come to be critical when the expressways cross the industrial region. A few roadways are worked on coal mining area, resulting in the claim that HMs contain coal dust on the top soil of the nearby regions. (Christoforidis and Stamatis 2009; Raj et al. 2017). The defilement brought about by HMs along the RSS is deteriorating and several scholars have realised in recent years. Beginning HMs in RSS may be acquainted with the deterioration of street surfaces, gasoline start in gas powered motors, oil spills from cars, tyre mileage, mining, dissolution of metallicores, corrosion of batteries, power plants, pesticides, and metallic components like radiators. (Khanet et al. 2011; Hassan and Ahmad 2015). In public express ways, anthropogenic contaminations from traffic and industrial exercises accumulate in street saved dregs and contain high groupings of HMs. Street stored dregs can spread by precipitation overflow or be re-suspended by the breeze in dry conditions, contaminating water, land and biological systems over time. (Jeong et al. 2020). Various researchers showed that the traffic-related contamination with Public expressways and in metropolitan region is a significant wellspring of HMs tainting in ecological examples like farm soil, street dust, and natural grasses. (Jeong et al. 2020).

HMs polluted soil also affect plant life. Metals such as lead (Pb), cadmium (Cd), arsenic (As), chromium (Cr), mercury (Hg) are toxic to plants and other living organisms at excessive concentrations (Wang et al. 2021). Cd is a much more toxic metal that affects plant growth, its metabolism, and condition (Divan et al. 2009). Lead is not an essential nutrient for plants; it was accumulated in plant roots and causes toxicity (Siedlecka et al. 2001; Ramazanova et al. 2020). Researchers worked on the risk evaluation in metropolitan soils contaminated by HMs. They found the HMs accumulation in the soils of 22 large cities of Kazakhstan, and finally results showed that HMs (Cd and Pb) accumulation in the industrial area is likely to have a human origin. Additionally, they conducted stochastic health risk assessments for both adults and children who were exposed to HMs in soil through cutaneous contact, ingestion, and inhalation. Due to its significant contribution (>75%) to the hazard index value, Pb was determined to be the most harmful pollutant. (Adimalla et al. 2020). further highlighted the issue of urban soil pollution in Sangareddy City, India, and found that the soils there were primarily moderately to severely polluted. They also observed that exposure to soil HMs frequently exposes both adults and children to health risks, including those related to cancer and other diseases.

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Aside from these, HMs upon openness by means of inward breath, ingestion or dermal contact can act both cancer-causing like well as non-cancer-causing impacts on people (Lu et al. 2017). A definitive danger of heavy metals in the soil is because of their relentless nature and their capability to become bio-gathered in food crop plants (He et al. 2021). When food crops polluted by heavy metals they can present unfriendly impacts upon the utilization of tainted vegetables and grains (He et al. 2021). The physico-chemical qualities of soil contrast from one spot to another and occasionally, contingent upon the parent material, because of coordinated impacts of normal elements, for instance, environment conditions and anthropogenic exercises, like emanation from industrial, homegrown and vehicular sources (Grossman and reinsch 2002). It is deeply grounded that dirt physico-chemical portrayal assumes a key part in investigating the piece of soil and assessing soil contamination (Pujar et al. 2012). Many examinations across the world have been directed to investigate the physico-chemical attributes of side of the road soil in various areas (Szwalec et al. 2020).

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Bockheim, (1974) gives a meaning of metropolitan soil: "as a soil material having a non-agricultural, synthetic surface layer more than 50cm thick that has been delivered by blending, filling, or by tainting of land surfaces in metropolitan and rural regions." This suggests that the soil has been upset in a piece of the profile, or maybe the whole profile might comprise of fill, and that man is the essential specialist of the unsettling influence. The blending, filling and tainting make a soil material that is not normal for its regular partner. Blending of soil material happens when the soil is scratched away, accumulated and yet again spread, or it very well might be shipped to one more area and spread as topsoil.

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Bockheim (1974) identified general characteristics of urban soils as follows

These are:

1. Considerable vertical and geographical diversity
2. Soil structure modification that causes compaction
3. A surface crust on bare soil that is often hydrophobic
4. Increased modified soil response is typical
5. Restricted water drainage and aeration
6. Nutrient cycling disruption and altered soil microbial activity
7. Contaminants and anthropogenic materials present (like heavy metals)
8. Altered soil temperature patterns

Heavy Metals Sources in the Environment

Sources of HMs in the environment can be both natural and anthropogenic. Two naturally occurring or geological sources of HMs in the environment include weathering of metal-bearing rocks and volcanic eruptions. The Earth's industrialization and urbanisation tendencies have increased the amount of HMs that are caused by humans in the environment. (Nagajyoti et al. 2010). The environment's HM contamination comes from a variety of human-made causes, such as mining, industry, and agriculture. Metals are released during the mining and extraction of different elements from their corresponding ores (heavy metals). Through dry and wet deposition, HMs that are discharged into the atmosphere during mining, smelting, and other industrial activities find their way back to the ground. When wastewaters, such as domestic sewage and industrial effluents, are discharged into the environment, heavy metals are released. The use of chemical fertilisers and the burning of fossil fuels both add to the human-caused release of HMs into the environment. Phosphate fertilisers are crucial when it comes to commercial chemical fertilisers' heavy metal content. Acidulation is typically used to create phosphate fertilisers from phosphate rock (PR). While sulfuric acid is used to acidulate single superphosphate, triple superphosphate (TSP) is acidulated using phosphoric acid (SSP). (Dissanayake et al. 2009). All of the HMs that were components of the phosphate rock are present in the finished product (Mortvedt 1996). Commercial inorganic fertilisers, especially those that include phosphate, have the potential to aid in the global transportation of HMs (Carnelo et al. 1997). Inorganic fertilisers used to add HMs to agricultural soils may cause groundwater to become contaminated (Dissanayake et al. 2009). Fertilizers with phosphate are very high

in dangerous HMs. The two primary routes for harmful HMs to enter the human body from phosphate fertilisers are illustrated here. (Dissanayake et al. 2009).

Phosphate rock → fertilizer → soil → plant → food → human body

Phosphate rock → fertilizer → water → Plant → human body

Anthropogenic sources of HMs include the use of fossil fuels for transportation, habitation, and industry. One of the main anthropogenic sources of HMs like Cr, Zn, Cd, and Pb is vehicle traffic. (Ferretti et al. 1995). In urban and metropolitan regions, higher levels of HMs that are significant for the environment have been found in the soil and plants growing beside highways. Emissions from coal combustion and other combustion processes are significant anthropogenic sources of HMs. (Merian et al. 1984). Cd, Pb, and As become moderately volatile after coal burning, whereas Hg becomes completely volatile. Among the anthropogenic sources of Cr are the steel, textile, leather tannery, and electroplating industries. (P. R. Palaniappan and S. Karthikeyan 2009). Around 50,000 t/year of Cr might be released into the atmosphere globally by burning coal, wood, and trash. (E. Merian 1984). Fertilizers typically also include considerable amounts of Cr (Krüger et al. 2017). Around 60,000 t/year of nickel may be produced worldwide by burning coal; the most of it would remain in the ash. (E. Merian 1984). The natural sources of Cd in the environment are volcanic activity and rock weathering, but nonferrous metal mining, notably the processing of Pb-Zn ores, is a human source (M. Hutton 1984). Approximately 7,000 t/year of Cd may be released into the atmosphere by burning coal, and Cd can also be released during the cremation of sewage sludge (E. Merian 1984). Excessive usage of chemical fertilisers also contributes to anthropogenic increases in Cd concentrations (Wang et al. 2015). Since P-containing fertilisers include Cd as a contaminant at concentrations ranging from trace quantities to 300 ppm on a dry weight basis, they may be a significant source of input for this metal into agricultural systems (C. A. Grant and S. C. Sheppard 2008). Acid batteries, outdated plumbing, lead shot used in game bird shooting, and other sources all release pb into the environment. Leaded gasoline combustion also contributes to the environmental contamination of Pb. Tetraethyl lead is still employed in some underdeveloped parts of the world even though it is no longer permitted to be used as an antiknock agent in gasoline.

Heavy Metals Sources in Agricultural Soils

Heavy metals are discharged from natural and anthropogenic action and status of soil tainting by poisonous metals. Harmful metals are two types; one which is in high amount in soil around plant and other one is less sum show the lack for plant. There are various sources of metals in the climate, for example

(1) Natural sources

(2) Anthropogenic sources(a) Mining, (b) Smelting and flying ash, (c) Fertilizers and agrochemicals, (d) Wastewater irrigation, (e) Sewage sludge application, (f) Livestock manures, (g) agricultural sources, (h) industrial sources, (i) domestic wastage and (j) atmospheric sources.

1. Natural Source: Geologic parent material or rock offshoots are the main natural sources of HMs. The stone nature and ecological circumstances, which actuate the lasting system, are dependent on the structure and grouping of HMs. The geologic kept materials typically have high groupings of Cr, Mn, Co, Ni, Cu, Zn, Cd, Sn, Hg and Pb. In any case, HMs concentration vacillates inside the stones. Soil development happens much of the time from sedimentary stone yet is just a little source of HMs since it isn't by and large or effortlessly endured. In any event, considerable amounts of Mn, Co, Ni, Cu, and Zn are added to the soils by a variety of igneous rocks, including olivine, augite, and hornblende. Shale has the highest concentration of Cr, Mn, Co, Ni, Cu, Zn, Cd, Sn, Hg, and Pb among sedimentary rocks, followed by limestone and sand stone. Natural sources of heavy metal have contributed a little sum in soil since it's not effectively accessible in soil

2. Anthropogenic Source:

Activities such as smelting and mining operations and agriculture have tainted body of land of the world. The expansion of HMs in surface soils is impacted by numerous human exercises, for example, modern creation, traffic, cultivating and water system and other huge areas of soil can be polluted by HMs set free from smelters, squander incinerators, and industrial wastewater and from the use of muck or civil manure, pesticides and fertilizers. Regardless of their sources in the soil, gathering of metals can debase soil quality, decrease crop yield and the nature of agricultural items and hence adversely influence the strength of animals, humans and the environment (Nagajyotiet al. 2010).

a. Mining: There are various sources of metal tainting in mining regions, including crushing, concentrating of minerals and tailings removal. The significant Indian coal mining regions are Jharia-Raniganj-Dhanbad belt

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falls under Eastern Coal Field Ltd., Singrauli-Bina in central part of India and Nayaveli lignite coal mineshafts are in Tamilnadu. Improper long-term mining exercises here had caused boundless metal contamination. It is accepted that around 25% farming soils and expanse of land of India are tainted with HMs.

b. Smelting and Flying ash: This environmental condition, according to Luo (2009), was responsible for between 43% and 85% of the total As, Cr, Hg, Ni, and Pb inputs to agricultural soils. In actuality, a significant majority of the heavy metal pollution in the air are caused by flying particles from activities that are mostly manmade, such as mining, electric generation, metal refining, and substance industries.

c. Fertilizers and Agrochemicals: HMs contribution to agricultural soils through fertilizers courses expanding worry for their expected gamble to ecological health. Phosphate fertilisers are often the main source of secondary metals among inorganic manures, and Cd concentration in phosphate fertilisers has also received a lot of attention. In some of the nations, phosphatic fertilizers have been utilized for significant stretches. Farming utilization of pesticides is one more source of weighty metals in arable soils from non-point source pollution.

d. Wastewater irrigation: Polluted sewage water system can diminish the water lack somewhat yet it can likewise bring a few harmful materials, particularly HMs, to farming soils and create serious ecological issues. This is especially an issue in vigorously populated developing nations where strain on water system water assets is very perfect. In Chhattisgarh, a state in central India, filthy ground water was used to irrigate the soil. Arsenic-related illnesses are common in this region. In this region, several industrial firms discharge waste water into drains on a regular basis without any or little wastewater treatment, which either pollutes rivers and streams or increases the pollution load of bio solids (sewage sludge). Streams and rivers are the main sources of water for irrigation in agricultural production, and bio solids are increasingly employed as soil ameliorants.

e. Sewage sludge application: Albeit the items in harmful metals in sewage sludge has additionally been notably diminished, and the majority of them are underneath the release standard of contaminations for metropolitan wastewater treatment plants because of the enormous expansion in how much wastewater treated, the sewage sludge delivered expanded quickly.

f. Livestock manures: Human's interest for meat, eggs and dairy raised incredibly throughout the last many years, because of their expectation for everyday comforts rising ceaselessly. HMs is introduced in domesticated animals' foods as added substances for health and gainful reasons. According to various reports, the contamination of HMs in poultry manures correspondingly increased with the usage of the feed additives. With an average input rate of 0.004 mg/kg/yr in the plough layer, Cd was given top priority among the metals in question in agricultural soils (0-20 cm) (Luo, 2009)

g. Agricultural sources: Agricultural soils in many regions of the world are marginally to respectably sullied by heavy metal harmfulness like Cd, Cu, Zn, Ni, Co, Cr, Hg, Pb, and As. This could be reasonable to long term use of phosphatic fertilizers, dust from smelters, sewage sludge application, agricultural waste and awful water system methods in agricultural lands. Agricultural polluted compost and pesticides sullied wastage are a significant source of heavy metals. The agro-chemical mixtures and compost applications are one of the fundamental reasons representing HMs enhancement. A few plants are likewise utilized as a phytoremedial, so in these plant tissues metals are gathered in various part of plant where, manure are utilized as compost in farming soil and doing tainting in soil.

h. Industrial sources: An exceptionally normal and significant source is heavy metal from mining and industrial wastes (vehicle, lead-corrosive batteries, manures, minerals refining businesses, petrochemical enterprises, paints, treated woods, nuclear energy stations and different ventures) representing the soil properties.

i. Domestic wastage: For the most part strong and fluid wastes are released from homegrown region in day to day existence, for example, sewage, wastewater, waste vegetable and other house hold squander.

j. Atmospheric sources: Common sources of environmental deposition in contaminated climatic region, for example, coal nuclear energy stations through release is fly debris particles. Vehicles are also a major source of HMs in soil after deposition such as lead (*Pb*), near highway, Agricultural soil contaminated by heavy vehicles. Soil Factors Affecting the Metal Availability in Soil (Harter and Lehmann 1983) proved that soil pH is the major factor interfering metal movement in soil. Organic matter and hydrous ferric oxide have been shown to decrease the availability of HMs by immobilization of these metals. Significant positive correlations have also been recorded between HMs and some soil physical properties such as soil moisture and water holding capacity of the soil. The density and type of charge in soil colloids, the degree of complexation with ligands, and the overall surface area of the soil are other elements that influence metal mobility in soil. The enormous limit and explicit surface regions given by soil colloids help in controlling the accumulation of heavy metals in natural

soils. Likewise, soluble convergences of metals in contaminated soils might be decreased by soil particles with high unambiguous surface region, however this might be metal specific. Soil properties, for example, air circulation, microbial movement and mineral structure have additionally been displayed to impact heavy metal accessibility in soils. Alternately, heavy metals might change soil properties particularly soil biological properties. Checking changes in soil microbiological and biochemical properties after defilement can be utilized to assess the level of soil contamination on the grounds that these biomonitoring devices are more delicate and results can be gotten at a quicker rate when contrasted with customary observing and testing of soil physical and chemical properties. Heavy metals influence the microbial populace, species variety and their exercises in soil. Metals' ability to kill microorganisms depends on the soil's temperature, pH, clay minerals, organic matter, inorganic anions and cations, and the metal's chemical makeup. (Becker and Asch, 2005).

Table 1. Regulatory Standards of Heavy Metals in Agricultural Soil (mg kg-1) pH

S.No.	Country	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
1.	Australia	20	3	50	100	1	60	300	200
2.	Canada	20	3	250	150	0.3	100	200	500
3.	China	20-40	0.3- .06	150- 300	50-200	0.8- 1.0	40-60	80	200- 300
4.	Germany	50	5	500	200	5	200	1000	600
5.	Tanzania	1	1	100	200	2	100	200	150
6.	Netherlands	76	3	180	190	36	100	530	720
7.	New Zealand	17	3	290	<104	200	N/A	160	N/A
8.	United kingdom	1.8	N/A	N/A	26	230	N/A	N/A	
9.	USA	0.11	0.48	11	270	1	72	200	1100

United States Environmental Protection Agency (USEPA, 2002), European Environmental Agency (EEA, 2007), Tanzania Minister of State (TMS, 2007), Canadian Ministry of the Environment (CME, 2009), Environment Protection Authority of Australia (EPAA, 2012), New Zealand Ministry for the Environment (NZME, 2012) and Environmental Protection Ministry of China (EPMC, 2015).

Table 2. Normal and Critical Range (mg g-1 dry wt.) of Important Heavy Metals in Soil

Elements	Normal range	Critical range
Bowen 1979	(Kabata-Pendias and Pendias, 1992)	
As	-	-
Cd	0.01-0.02	3-8
Hg	-	-
Pb	2-300	100-400
Sb	-	-
Co	-	-
Cr	5-1500	75-100
Cu	2-250	60-125
Fe	-	-
Mn	20-10000	1500-3000
Mo	-	-
Ni	2-750	10-100
Sr	-	-
Zn	1-900	70-400

Heavy metals remediation

The most economical method of pollution control is always prevention. In the unfortunate event that heavy metal contamination occurs in soil on agricultural land or in urban areas, remedial procedures must be put in place to lessen the potentially dangerous effects.

In-situ remediation techniques for heavy metal-contaminated soils

In-situ remediation **doesn't** need unearthing and transport of the contaminated soil to offsite treatment facilities and consequently, soil aggravation is minimized, openness of labourers and the encompassing public to the pollution is reduced, and the treatment cost might be altogether decreased. However, individual field circumstances including weather, soil permeability, contamination depth, and possible chemical deep leaching must be properly taken into account. (Olexsey and Parker 2006).

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a. Surface capping

The goal of surface capping is to simply frame a stable, protective surface over the contaminated area by covering it with a layer of waterproof material. This control based procedure **isn't** really a soil "remediation" technique, as no endeavours are made to eliminate the heavy metal pollutants or possibly decrease their reactivity in the soil. Nevertheless, the strategy works productively to dispose of the gamble of openness to the polluted soil through skin contact or coincidental ingestion. The surface cap serves further as an impermeable boundary to surface water penetration, keeping soil pollutants from further diffusing to surface water and groundwater. The covered soil, in any case, loses its normal ecological capabilities particularly in supporting plant development. The treated region might be utilized for other common purposes as a parking area or a game field (NJDEP 2014). Determination of a proper covering framework is site explicit, changing with site qualities and healing targets. Single-layer covers or multi-facet frameworks can be utilized, with numerous decisions of the covering materials including clay, concrete, asphalt, and high-thickness polyethylene.

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The surface cover should reach 60–90 cm beyond the horizontal extent of the pollution location while maintaining acceptable structural strength and dynamic stability. (Rumer and Ryan 1995). It is common practise to create water control structures including ditches, dikes, and slopes to direct runoff and drainage from surface caps. In multilayer cap systems, vegetation can be established by covering the impermeable cover layer with soil.

A treatment option for heavily contaminated soils is surface capping. (e.g., Igeo > 3). The method is applicable for correcting small areas (e.g., <2,000 m²). Otherwise, construction the capping surface becomes challenging. Groundwater table depth and seasonal variation at the restoration site, as well as neighbouring hydrogeological features (e.g., ponds, runoff) that could affect the stability of the cap require careful study. When placing a cap on sloped terrain, the risk of the cap sliding 155 to be considered. The community's approval must be considered if the cleanup site is close to residential areas, parks, or walking paths. Overall, surface capping is a quick, easy, and efficient way to reduce the danger of soil contamination. It is the best option in terms of project duration and cost, but it is the worst option in terms of changes to soil ecosystem function and land use. The technique has been used frequently to clean up small patches of soil that have been contaminated with heavy metals and organic contaminants. (NJDEP 2014). The necessary engineering design, materials, manpower, and follow-up operations all go into the price of a surface capping job. (e.g., inspection, maintenance). The recent cost ranges from \$20 m⁻² to \$90 m⁻² in the U.S. (NJDEP 2014).

b. Encapsulation

Encapsulation is a corrective technique also known as "barrier wall," "cutoff wall," or "liner." an alternative to surface capping is paralleling. The method involves enclosing contaminated soil in a physically barrier system that is appropriately built and made up of low permeability caps, enclosing underground barriers, and, in rare circumstances, barrier floors. Pollutants are contained and isolated at contaminated sites, preventing their spread off-site and human exposure to them while they are present. (Khan et al. 2004; Meuser 2013). The low permeability caps, which are often clay layers or synthetic textile sheets, reduce surface water infiltration and hence stop toxins from leaking into groundwater. The underground impermeable barriers prevent horizontal migration of the contaminating source through subsurface interflow and possible diffusion.

Constructing subsurface vertical impermeable walls at contaminated sites is the fundamental difficulty in encapsulation. Slurry walls, thin walls, sheet pile walls, and injection walls are only a few of the construction techniques that have been created. (Bradl and Xenidis 2005; Meuser, 2013). For instance, in the slurry wall approach, a trench is initially dug in the earth to the required depth using a grab bucket or trench cutter. The trench is subsequently filled with a cement-bentonite-water slurry, which hardens into a wall that is 0.4–1 m thick. Glass tiles, sheet piling, and HDPE (high density polyethylene) membranes can all be placed into the still-liquid slurry to boost the wall's strength and impermeability. The wall can be built in successive panels over time, but to maintain the integrity of the wall, the watertight contact between the panels must be guaranteed. In order to create a thin wall, a pressure jet is used to vibrate a large steel beam into the ground. The trench is subsequently filled with a clay-cement-water slurry to form a 0.15-m-thin wall. The structure's impermeability is increased by the soil's compaction during trench preparation. Alternately, impermeable sheet pile walls can be

constructed using steel/aluminium sheets, precast concrete plates, or wood planks that are driven into the ground and secured with locks. More frequently, grouting materials like cement suspension and synthetic resins are injected into the boreholes through a high-pressure jet, and after the grouting slurry solidifies and fills the soil pores between adjacent boreholes, a "soilcrete" injection wall forms. Boreholes are typically dug to the desired depth in the ground using rotary casing. (Bradl and Xenidis 2005). Low hydraulic conductivity ($<10^{-7}$ cm s $^{-1}$), low shrinkage, acceptable strength, and long-term endurance are characteristics of high-quality barrier walls. (Meuser 2013). Encapsulation is limited to shallow, small-area contaminated locations, such as surface capping. When other affordable, excavation-200 and-treatment remediation options are not available, the technology is frequently chosen to manage sites contaminated by radionuclides, asbestos, polycyclic aromatic hydrocarbons (PAHs), heavy petroleum hydrocarbons, and mixed wastes. (Meuser 2013). It is especially suitable for locations with high seasonal groundwater tables, when vertical barrier walls are built below the water table to stop additional contamination of the groundwater. The price of soil encapsulation varies depending on the level of contamination and the geology of the site, but it is reportedly more expensive and may double the price of surface capping. (National Research Council 1997).

c. Electrokinetic extraction

By using electrical adsorption, electrokinetic extraction purges heavy metals from polluted soils. When low-density direct current (DC) electricity is provided using electrodes buried in the ground, cations in the contaminated soil's solution phase move to the cathode and anions move to the anode due to the electrical field's attraction force. The following removal of the concentrated metal impurities at the polarised electrodes involves electroplating, (co-)precipitation, solution pumping, or ion exchange resin complexation. (FRTR 2012).

Since the late 1980s, electrokinetic extraction has been studied for removing contaminants from soil (Alshawabkeh 2009). The method can be used to decontaminate both water-saturated and water-unsaturated fine-grained soils since it has a low hydraulic conductivity. However, the efficacy of electrochemical remediation depends on the particular field conditions that are present, such as the types and amounts of contaminants present, the type of soil, pH, and organic content. (Figueroa et al. 2016). The duration of electrokinetic remediation might range from a few days to several years, depending on the overall speed of the metal ions moving through the soil. Metal ions migrate primarily through electroosmosis (the movement of water from anode to cathode; even non-ionic species can be transported along with the water flow caused by electroosmosis), electromigration (the migration of ions to the counterpart electrode), electrophoresis (the migration of charged colloidal particles), and diffusion under a DC electric field (transport induced by concentration gradients) (Page and Page 2002). The kind of metal, mobility of metal ions (by charge density and hydrated radius), aqueous metal concentration, soil type, soil structure, soil moisture content, and soil solution chemistry all affect the direction, speed, and amount of heavy metal migration. The potential for sorption, precipitation, and dissolution over the course of the migration (Virkyte et al. 2002). The migration velocity of a metal ion in an electrical field can be predicted by the Helmholtz–Smoluchowski equation (Karim 2015)

$$\mu_e = -\frac{z\zeta}{\eta}$$

In soils, heavy metals are mainly found as precipitates and adsorbed forms. Desorption/dissolution and then transport are steps in the electrokinetic extraction of heavy metals. Chemical additions are often required to aid in the mobilisation of sorbed metals when the concentration of heavy metals in the soil solution falls below the soil sorption capacity. In order to enhance the movement of low-concentration metal ions, more energy must be consumed. Diethylenetriaminepentaacetic acid (DTPA), nitrilotriacetic acid (NTA), ethylene-diamine-tetraacetic acid (EDTA), ethylene-diamine-disuccinic acid (EDDS), ethylene-diamine-disuccinic acid (EDDS), acetic acid (CH₃COOH), citric acid ((HOOC-246 CH₂)₂C(OH)(COOH), and potassium (KI). These additives (enhancement fluids) exhibit various levels of metal species mobilisation efficiency in soil. (Zhang et al. 2014; Sivapullaiah et al. 2015; Song et al. 2016). Water around the electrodes hydrolyzes under the influence of a DC electric field to create a low pH, high redox potential region near the anode. (H₂O - 2e⁻ → 2H⁺ + 1/2O₂) and a high pH, low redox potential area at the cathode (2H₂O + 2e⁻ → 2OH⁻ + H₂), causing a reducing base front and an oxidising acid front to steadily move in the direction of the opposing electrode. As a result, the profiles of pH, redox potential, electrical conductivity, and solution chemistry across the positive and negative electrodes are transient, nonlinear, and nonuniform (Alshawabkeh 2009). The surface charge of soil particles and the mobility of metal ions are particularly affected by pH changes. Metal ions that have been sorbed can be mobilised by the created acidic conditions. Further preventing the production of metal hydroxide and carbonate precipitates is an acidic environment.

However, if the soil has a high buffering capacity, the in-situ acidification may not be sufficient. Additionally, the produced base front results in the precipitation of metal ions, delaying their final arrival at the cathode (Reddy 2013). Evidently, electrokinetic soil remediation requires artificial acidity (Bahemmat and Farahbakhsh 2015). However, external addition of inorganic acids (such HNO₃) might be expensive and is not acceptable in terms of the environment. In order to maintain ideal remediation conditions, water or chemical solution (such as 0.1 M EDTA or acetic acid) is often continually fed at the anode; polluted water is removed at the cathode by pumping (Alshawabkeh 2009). Minor electrolytic gases, such as Cl₂ and H₂S, are created at the electrodes, but if they are allowed to constantly bubble out without adhering to the electrode surfaces, they have no impact on the electrokinetic process. (Virikutyte et al. 2002; Niroumand et al. 2012).

Heavy metals, anionic contaminants, and polar organics in soil, sediments, sludge, and dredge are electrokinetic extraction targets. Testing has been done on soils that contain one or more of the heavy metals Pb, Cr, Cd, Co, Ni, Cu, Zn, Hg, and Ur. By eliminating the water-soluble and exchangeable fractions of metal pollutants, the method is most efficient for remediating saturated or partially saturated (for example, moisture content 15–25 percent), low permeability, low electrical conductivity, fine-textured soils (Reddy, 2013). Gravels, mineral deposits, and metallic objects in soil are insulating and conducting materials that impair the efficiency of electrokinetic extraction. In actuality, arrays of inert electrodes composed of ceramic, carbon, graphite, titanium, stainless steel, or plastic are set in ceramic wells in the polluted soil at spacings of 1.0 to 1.5 m, with imposed DC current at 1.0 to 1.5 V cm⁻¹ or 100 to 500 kWh m⁻³. (FRTR 2012).

At the cathode, there are pumps and treatment facilities set up to extract and handle polluted water. The system might contain several anode/cathode pairings, numerous anodes, or a single cathode deployed in a circular or parallel arrangement. The distribution and strength of the created electrical field are influenced by the size, shape, and placement of the electrodes, which has an effect on the effectiveness of the therapy. (Turner and Genc 2005). In addition to the ideal electrode configuration, other actions can be taken to increase the efficiency of metal removal, including lengthening the treatment period, increasing the electric potential gradient, switching the electric field's mode (from continuous to periodic), and incorporating cation/anion exchange membranes into the electrodes. (Reddy 2013). With the level of pollution and the field circumstances, the overall cost of electrokinetic soil remediation varies greatly. According to 2012 estimates from the U.S. Federal Remediation Technologies Roundtable (FRTR), the cost averaged \$117 m⁻³ in the range of \$26-295 m⁻³, including \$15 m⁻³ soil for the electricity consumption. (FRTR 2012).

Electrokinetic remediation is currently in the early stages of development. The approach is used in a handful of demonstration and pilot-scale projects, although full-scale implementations remain uncommon (Hansen et al. 2016). According to a U.S. pilot research, electrokinetic therapy for 30 weeks reduced a Pb-contaminated site's soil Pb level from 4500 mg kg⁻¹ to under 300 mg kg⁻¹ (FRTR 2012). Another U.S. pilot investigation found that despite electrokinetic extraction taking place for 22 weeks, substantial levels of Cr and Cd were not removed from the contaminated soil. This is most likely because the soil included a lot of NaCl and metal sulphides. (Geoengineer 2013).

d. Soil flushing

By circulating an extraction solution through the soil, soil flushing removes pollutants from the soil in-situ. The recovery, reuse, treatment, and disposal of the extraction fluid follow. The method may be used on uniform, coarse-textured soils with high permeability (CLU-IN 2017). The extraction fluid is often injected or absorbed into the soil during soil flushing. The extraction fluid needs to be made according to a certain formula in order to remove heavy metals from soil successfully. Testing of several chelating and acidic solutions has shown that EDTA is the most efficient agent. In batch trials, (Wuana et al. 2010) discovered that EDTA outperformed citric acid and tartaric acid in removing heavy metals from a fortified loamy sand (pH 6.1, organic matter (OM) content 8.7%) at 0.01 M and 1:25 soil/solution ratio. The solutions showed that mobilisation efficiency varied with coexisting metal species: Ni > Zn > Cd > Pb. Citric acid and tartaric acid were ineffective for mobilising organic matter-bound and residual metal fractions, according to a sequential extraction analysis of the results. EDTA, however, mobilised all non-residual metal fractions. In comparison to water, surfactants, and cyclodextrin, (Reddy et al. 2011) found that 0.2 M EDTA was the most effective extraction fluid, 314 flushing out 25–75 percent of the Cu, Zn, and Pb in industry-contaminated loam sand (pH 7.0, OM 11.1 percent) columns. When used to remove Cu and Ni from a pH 5.0 clay loam, the biodegradable chelating agent chitosan (pH 3.3) outperformed EDTA (pH 3.1) at 2.0 g L⁻¹. (Jiang et al. 2011). Pb had the highest removal effectiveness (75%) while Cu had the lowest (25 percent). Though technically straightforward, installing solution collection wells or subsurface drains may be difficult and expensive. Groundwater is frequently removed to recover the flushing elutriate when the water table is shallow. For soils with high cation exchange capacity (CEC), high

buffering capacity, high OM, and high clay concentrations, the metal extraction efficiency is often poor. The method has been shown in the literature to have the capacity to remove Pb from acidic sandy soils, Cd from low CEC, low clay, and moderately acidic soils, Cr (VI), and As from low iron oxides, low clay, and high pH permeable soils. (Shammas 2009). The variety of the soil and the arrangement of the layering have an additional impact on the technique's application. The cost of the soil flushing treatment was projected to be between \$20 to 104 per m³ of soil, with the price rising as the water table rose and soil permeability decreased (Iturbe et al. 2004; FRTR, 2012). The approach, which involves flushing surfactant solutions through polluted areas, has been used increasingly often to eliminate organic contaminants. The main objective of these soil remediation projects was to remove organic contaminants, and at three of the sites (Lipari Landfill, NJ; Sprague Road Groundwater Plume, TX; and United Chrome Products, OR), also the heavy metals Cr, Hg, and Pb. A list of the in-situ soil flushing projects in North America can be found in (USEPA 2012).

e. Chemical immobilization

By adding chemical agents to the initial medium to solidify the soil or change the mobile pollutant fractions (i.e., soluble and exchangeable forms) into precipitates and/or strongly sorbed moiety, in-situ chemical immobilisation, also known as in-situ solidification/stabilisation (S/S), aims to trap or immobilise pollutants in the contaminated soil. Contaminants in soil are neither extracted nor removed by chemical immobilisation. Instead, heavy metals' solubility/mobility and concentrations in soil pore water are greatly reduced, reducing their potential transfer to aquatic life, plants, and microbes. (Tajudin et al. 2016).

Both in-situ and ex-situ techniques can use the soil remediation technique known as solidification. In order to turn contaminated soil into a solid block, in-situ solidification involves adding a binding agent to the soil, most frequently cement, asphalt, fly ash, and/or clay. If contaminants are deeply buried in the soil, a crane fitted with an injector head and a large mixer can be used to inject binding slurries into the subsurface and mix the waste with it. Because the solid block is water-impermeable, the enclosed contaminants are not leachable (Tajudin et al. 2016). However, if the solid block's integrity is compromised over time by uncontrolled mechanical disturbance and natural weathering, the imprisoned pollutants can become mobile once more (FRTR 2012). Future uses of the site could potentially be restricted. Since the 1980s, solidification has been a widely used technology in the United States. More than 60 locations with heavy metal contamination have been treated using it in-situ (USEPA, 2016a). In comparison to alternative treatment methods, a solidification project operates on average for 1.1 months. The pollutants are not destroyed nor eliminated by solidification. The cemented portions could prevent a subsequent, more thorough repair. Solidification is thus the final resort for soil restoration and should only be used in cases when other techniques are not feasible. Since solidification needs a significant amount of binding agent, its availability and transportation costs have a significant impact on its usefulness. The total cost of solidification varies depending on the site and can reach \$1500 m⁻³ (\$520 m⁻³ on average in the U.S. in 2012). This cost includes material, drilling, and mixing costs. (FRTR 2012). While immobilising pollutants, stabilisation (also known as "in-situ fixing") does not solidify the soil. Other than binding agents, stabilising chemicals are added to contaminated soil as precipitation reagents in order to restrict the mobility of the heavy metals by causing physiochemical interactions (Tajudin et al, 2016). For this, a variety of substances have been tested, including clay, carbonates (such as lime), phosphates (such as bone meal, ammonium phosphate, apatite, and hydroxyapatite), alkaline agents (such as fly ash, and calcium hydroxide), and minerals containing iron. (e.g., bauxite, red mud, goethite, greensand, molecular sieves, palygorskite, silica gel, vermiculite, and zeolites), and organic matter (e.g., chitosan, starch xanthate, peat, compost, manure, activated carbon, and biochar) (Basta and McGowen 2004; Gray et al. 2006; Kumpiene et al. 2008; Farrell and Jones, 2010; He et al. 2013; Bolan et al. 2014; Ali et al. 2017; Seshadri et al. 2017). These soil supplements generally work by inducing a number of physiochemical processes, such as precipitation, surface precipitation, coprecipitation, complexation, and surface adsorption, which limit the bioavailability and leaching potential of heavy metals. However, through distinct processes, the individual compounds were selectively efficient in immobilising certain metal species. For instance, (Castaldi et al. 2005) showed that zeolite (0.02 mm) sprayed at 100 g kg⁻¹ was the most successful treatment for lowering Cd uptake by lupin plants from a polluted sandy loam (pH 4.4); but the former treatments were more effective for reducing Pb and Zn uptake. By generating the thermochemically stable mineral pyromorphites (Pb₅(PO₄)₃(Cl,F,OH)), phosphate-based treatments might successfully lower the bioavailability and leachability of Pb in polluted soils for more than 10 years. (Tang et al. 2009). Materials that include phosphates and carbonates are the most promising for effectively stabilising heavy metals in polluted soils. These two elements are frequently used on agriculture as a fertiliser or an acidity conditioner since they are generally accessible and inexpensive. By combining treatment agents with the contaminated soil at the right rates and at the right times, which were previously identified through field studies,

in-situ chemical stabilisation is carried out. To allow for free soil penetration, treatment chemicals that are water soluble might be sprayed in aqueous solutions over the site. Typically, insoluble treatment ingredients are distributed across the site's surface before being ploughed in. Additionally, soil can be injected with a suspension of chemicals in fine powder form. Crops can be grown in the remedied soil since plant absorption of the metal pollutants has been reduced to a risk-free level. In less polluted farmed soils (like Igeo 3), chemical stabilisation is a useful, economical way for temporarily "fixing" heavy metals. The chemical stabilising effect must be periodically checked and assessed since heavy metals are not eliminated. For effective soil remediation, stabilising chemicals must be "well-mixed" with polluted soils. Since well-mixing cannot be guaranteed in large-scale field operations, the USEPA has not used this method for cleaning up Superfund sites.

f. Phytoremediation

In order to stabilise heavy metals into a harmless state (phytoimmobilization and phytostabilization) or remove them (phytoextraction and phytovolatilization), green plants are grown in polluted soils as part of phytoremediation (Mahmood et al. 2015). This plant-based technology is easily operated, looks better, is practical financially, and is generally recognised. Phytoremediation often enhances the physical, chemical, and biological quality of polluted soils, in contrast to physical and chemical treatments that permanently change soil attributes.

Plants have been studied and utilised to alleviate soil and wetland heavy metal pollution since the 1970s. The technique for cleaning up polluted sites was first used by the government and business in the 1980s. The technology has undergone extensive research and quick development throughout the years. The concepts and practicability of phytoremediation of metal-contaminated soils have been thoroughly reviewed. (Van Nevel et al. 2007; Vameralli et al. 2009; Pinto et al. 2015; Sarwar et al. 2017). Generally speaking, phytoremediation may be divided into two basic categories: Phytoextraction, which involves plants absorbing heavy metals from the soil and accumulating them in their shoots and leaves, and phytostabilization, which involves plant roots immobilising heavy metals in the soil. In phytoextraction, heavy metals are extracted from soil by macrophytes called hyperaccumulators that can accumulate more than 10 g kg⁻¹ of Mn or Zn, more than 1 g kg⁻¹ of As, Co, Cr, Cu, Ni, Pb, Sb, Se, or Tl, and more than 0.01 g kg⁻¹ of Cd in their aerial organs without experiencing phytotoxic harm. (Verbruggen et al. 2009). Accumulator plants, like *Astragalus racemosus*, may release gaseous species of the metal(loid)s As, Hg, and Se into the environment. It is known as phytovolatilization. There are now 721 plant species known to be metal hyperaccumulators. (Reeves et al. 2017). These plants can withstand high levels of heavy metals, thrive in soils rich in metals, and have unique capacities to efficiently absorb specific metal ions from the soil, move the metals from the roots to the shoots, and detoxify and sequester the metals in the tissues of the leaves. For instance, the native New Caledonian tree *Sebertia acuminata*, which is a Ni hyperaccumulator, may store Ni in its latex up to 26 percent of its dry mass. (Jaffré et al. 2013) Tobacco (*Nicotiana tabacum* L.) is a Cd hyperaccumulator. *Arabidopsis halleri*, *Thlaspi goesingense*, and *Sedum alfredii* are Zn hyperaccumulators. *A. halleri*, *S. alfredii*, *Thlaspi caerulescens*, and *Thymus praecox* are both Cd and Zn hyperaccumulators (Rascio and Navari- Izzo, 2011; Yang et al. 2017a).

Successful phytoextraction is defined as the removal of contaminants from contaminated soils to a level that complies with environmental laws at a cost that is less expensive than the cost of employing other alternative approaches or doing nothing. To estimate the time required for successful phytoextraction, the following equations are commonly used (Chandra et al. 2017).

$$M = Adp_i \Delta C$$

The significant technological obstacles that hinder the practical use of heavy metal hyperaccumulators in soil remediation have not been resolved through research and development. Field soil has geographical heterogeneity, and plant growth varies over time. The detected hyperaccumulators often have shallow root systems, moderate growth rates, and poor biomass yields. They are also restricted to their natural environments and metal-selective. There is typically a dearth of understanding about how to cultivate hyperaccumulators. (Chaney and Baklanov. 2017). Additionally, there is a correlation between phytoaccumulation of heavy metals and the concentration that is present in the soil. Heavy metals exhibit linear or even logarithmic declines in soil bioavailable concentration with subsequent croppings, and subsequently in the phytoextracted quantity. (Van Nevel et al. 2007). Infection from pests or nutrient deficiency may also cause a decline in the plant biomass output over time. These criteria all show that phytoextraction is an ineffective, unusable method. It would take 15 years to use hyper accumulators to remove 1 mg kg⁻¹ of Cd from a polluted soil, even in theory. (Li et al. 2012). In remedial techniques, the duration is obviously unsatisfactory (expected: 10 years). Numerous strategies have been put out to quicken phytoextraction, including the improvement of chelating agents and

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plant genetic modification. Metal chelates, however, are resistant to biodegradation and may seep into deep soil and groundwater (e.g., with EDTA and DTPA). In phytoextraction, artificial chelate aid should not be taken into account. (Evangelou et al. 2007). The development of genetically modified hyperaccumulators may need a lot of time and effort (Fansani et al. 2017). To reach practical viability, the existing phytoextraction method has to be significantly improved. Phytoextraction may make the remediation aim more achievable by changing it from lowering total soil metal concentrations to lowering the labile, bioavailable metal pool. (e.g., water soluble and exchangeable forms). In this situation, it is necessary to evaluate the bioavailable pool's long-term replenishment kinetics. Fast-growing plants have recently been investigated for heavy metal phytoextraction, including hybrid poplar (*Populus* spp.), shrub willow (*Salix* spp.), and Indian mustard (*Brassica juncea*). (Mleczek et al. 2010; Pinto et al. 2015). Despite not being metal hyperaccumulators, these plants have a substantially larger production of aerial biomass and have comparable total metal extraction abilities. More importantly, the biomass that is generated may be used as feedstock for biofuel. Phytoextraction regions should be enclosed to reduce any ecological dangers and stop wildlife from consuming the hyperaccumulator plants, which might introduce heavy metals into the food chain. After harvest, phytoextraction biomass should either be landfilled or burned, with the ashes then either treated to recover the metals. Uses for human or animal consumption are forbidden. (Ali et al. 2013; Fedje et al. 2015). If trees are utilised to extract metal, the roots must be dug up and disposed of once the operation is complete. (Pinto et al. 2015).

Phytostabilization, also known as phytoimmobilization, is an alternative strategy that uses plants to immobilise heavy metals in soil through root absorption, root adsorption, exudate complexation/precipitation, rhizospheric reduction, and soil stabilization. Heavy metal tolerance, high root biomass production, and little heavy metal translocation from roots to aboveground tissues are all characteristics of phytostabilization plants. The plants Sibth (*Agrostistenuis*), Red Fescue (*Festucarubra* L.), wiregrass (*Gentianapennelliana*), thatching grass (*Hyparrheniahirta*), Syrian bean-caper (*Zygophyllumfabago*), and hippo grass (*Vossiacuspidate*) are excellent candidates for phytostabilizing soils contaminated by Pb, Zn, Cr, and Cu (Yoon et al. 2006; Galal et al. 2017; Radziemska et al. 2017). Pb, As, Cd, Cr, Cu, and Zn mobility in contaminated soils has been shown to be reduced by phytostabilization, which has also been shown to stabilise disturbed metalliferous sites by successful revegetation. It acts as a stopgap measure for reducing the ecological concerns associated with polluted sites, particularly in places where natural flora is not present due to excessive metal concentrations. However, the method cannot be used in highly polluted areas where plant growth and survival are seldom viable. The method is frequently used in actual practise in conjunction with chemical stabilisation to recover defunct mining sites. Chemical soil additions (such as compost, lime, or phosphates) improve the environment for the establishment of phytostabilization plants by lowering the bioavailability and biotoxicity of the heavy metals present in the soil. (Chaney and Baklanov 2017).

Large, dispersed, and superficially contaminated regions with fine-textured, high-organic matter-content soils respond very well to phytoremediation (Chaney and Baklanov 2017). The method is still in its infancy at the moment. To comprehend the interactions between the rhizosphere's soil, metal chelates, and plants as well as how plants absorb, move, and accumulate heavy metals, further study and development is required. Numerous environmental factors, such as soil characteristics (such as pH, buffering ability, texture, clay minerals, organic matter content, fertility, and cation exchange capacity), contaminants (such as metal species, content, and speciation), chemical amendments used (such as type, rate, and application method), plant characteristics (such as species, growth stage), climate (such as precipitation, temperature), and geography, affect the success of phytoremediation (e.g., slope and aspect) (Vamerali et al. 2009; Chaney and Baklanov 2017). Over 100 confirmed soil heavy metal treatment pilot/field operations employing the phytoremediation technique have been conducted globally (USEPA, 2016b). 1.6 ha of land were planted with hybrid poplar, willows, and Eastern gamagrass as part of the 317/319 Area Soil Remediation Project in Lemont, IL, USA, which began in 1999 with an initial budget of \$1.2 million. By phytoextraction, phytostabilization, and phytodegradation, As, Pb, Zn, and organic contaminants were removed from the soil.

g. Bioremediation

Using microorganisms rather than plants to clean up contaminated soil is called bioremediation. The process is most frequently used to purge organic contaminants from soil and groundwater (FRTR, 2012). Along with valence transformation (e.g., Cr(VI) to Cr(III), SeO₄²⁻ to Se), biosorption (to the surface of the cell), extracellular chemical precipitation (e.g., by S²⁻ from sulfur-reducing bacteria), and volatilization, microorganisms may also detoxify metals (e.g. dimethylselenide, trimethylarsine and Hg vapor) (Garbisu and Alkorta 2003). In order to increase the solubilization of heavy metals prior to extraction, bioremediation is frequently used in conjunction with other methods, such as soil flushing and phytoextraction, in the cleanup of

heavy metal-contaminated soils. For instance, *Alcaligenes eutrophus* was discovered by Diels et al. (1999) to create siderophores capable of forming complexes with metals; the addition of the bacteria greatly enhanced the water extraction of Cd, Zn, and Pb from a sandy soil. The presence of the iron-reducing bacterium *Desulfuromonas palmitatis* greatly enhanced the release of As in a calcareous soil (Vaxevanidou et al. 2008). Many bacteria (e.g., *Bacillus subtilis*, *Torulopsis bombicola*) could produce biosurfactants such as surfactin, rhamnolipids, sophorolipids, aescin, and saponin to solubilize metals in soils (Acikel 2011). Certain rhizosphere microbes promote the tolerance of plants to heavy metals and enhance their growth in contaminated soils (Mishra et al., 2017). It is possible to remove mercury from soil in-situ via microbial enhanced volatilization, in which bacteria convert methyl mercury into Hg(II) and then decrease it to Hg(0) (Dash and Das 2015). Heavy metal hyperaccumulation-capable genetically altered microbes have been created. (Ruta et al. 2017). Yadav and his team provide a list of the studied bacteria, algae, yeasts, and fungi that may be helpful in soil heavy metal cleanup (2017a). The term "nanobioremediation," which describes methods for removing heavy metals and organic pollutants from wastewater and soil using nanoparticles (such as nano iron, nano silicates, and nanosulfonic acid) produced by specific plants, bacteria, algae, fungi, and bacteria under controlled circumstances, has just recently come into use. (Yadav et al. 2017b). In actual practice, spray irrigation or infiltration galleries are used to inoculate the polluted soil with certain microorganisms. If the toxins are deeply buried in the soil, injection wells can be employed. To promote microbial activity and improve the bioremediation process, nutrients, oxygen, and other amendments are often provided in combination. The method has been used to remediate organic contaminants in soils and aquifers, such as petroleum, non-halogenated volatile organic compounds, and PAHs (FRTR 2012). There have never been any reports of heavy metal-contaminated soil treatment employing bioremediation.

Ex-situ remediation techniques

Ex-situ soil remediation entails removing soil from the contaminated site, transporting the contaminated soil to a facility for off-site treatment, and disposing of the treated soil in designated areas. Ex-situ treatment is more expensive than in-situ remediation in terms of soil removal, transport, disposal, and site refilling, but it may be regulated and expedited, producing greater outcomes in less time.

a. Landfilling

The simplest method of soil remediation, known as "dig and haul," involves moving the contaminated soil from its original location and dumping it in a secure landfill. A designed construction with impermeable liners, leachate drains, and dike enclosures is a secure landfill. To avoid potential leaks and groundwater contamination, the facility has twin liners (a plastic layer and a clay layer) as well as a leachate collecting and monitoring system. The top cap/liner system keeps surface runoff away from the fill and reduces rainwater infiltration. Governmental rules and regulations must be adhered to during the design, construction, and usage of a secure landfill. The disposal of garbage is a tried-and-true method for clearing up hazardous waste sites. Before 1984, it was the most popular way to dispose of trash in the United States. The entire cost of landfilling soil in the United States varies from \$300 to \$500 per tonne, depending on how far the polluted site is from the secure landfill (FRTR 2012). Landfilling should only be taken into consideration for soils removed from high-contamination locations, or "hotspots," in order to lower the disposal cost.

b. Soil washing

Soil washing is a physical and chemical procedure that uses ex-situ washing of the soil with specially prepared solutions to remove heavy metals from polluted soil. When in use, soil removed from a contaminated site is first crushed and screened to get rid of coarse items like stones, wood, and plastic residues. Magnets are used to extract magnetic elements from the soil. By sonication or mechanical agitation, the screened soil (e.g., 5 mm) is completely mixed with a washing solution before being sieved or hydrocycloned to separate the coarse sand and gravel fraction (>0.05 mm) from the fine silt and clay fraction (0.05 mm). After water washing, the coarse fraction, which is less polluted, is often returned to the original location. The clay and silt particles suspended in the washing solution are removed by settling, cleaned with water, and then put back where they came from. The wasted washing solution and rinse water are recycled, transferred to another location for reuse, or dumped at a wastewater treatment plant. Prior to landfilling, the sludge from the wastewater treatment process is further processed by solidification and stabilisation. By modifying the soil's acidity, the solution's ionic strength, its redox potential, or its complexation, washing solutions are used in soil washing to mobilise heavy metals. An ideal washing solution should be nontoxic, biodegradable, and greatly increase the solubility and mobility of heavy metal pollutants while interacting little with soil components. To create efficient washing solutions, a variety of chemicals have been tested, including hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, fluorosilicic acid, formic acid, acetic acid, oxalic acid, citric acid, tartaric acid, polyglutamic acid, EDTA,

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(2) Give examples of bioremediation, biostimulation, bioaugmentation

DTPA, NTA, EDDS, carbonate/bicarbonate, sodium hydroxide, calcium chloride, ferric chloride, etc. (Moutsatsou et al. 2006; Fedje et al. 2013; Zhu et al. 2015; Alghanmi et al. 2015; Bilgin and Tulun 2016; Yang et al. 2017b). The pH, soil texture, and level of organic matter all had an impact on how well a washing solution removed metals from different metal species (FRTR 2012). Overall, over a variety of heavy metals and soils, hydrochloric acid, EDTA, and subcritical water showed the best washing efficiency. The ideal washing circumstances, such as the right washing solution concentration (e.g., 0.1–1.0 M HCl or 0.05–0.2 M EDTA), The soil/solution ratio (for example, 20–50 g L⁻¹) and agitation time (for example, 0.5–5 h) must be determined by small-scale experiments. Sequential washing using various solutions might be used if a single washing solution cannot be created to effectively remove complex pollutants from dirt. Trommels, screens, hydrocyclones, and centrifuges, for example, were created for the processing of minerals and may be used for soil cleaning. In the 1980s, the United States and certain European nations, including Sweden, developed mobile soil washing devices to lower the expenses associated with transporting dirt. These nations used the device in field settings to remove polluted soils (FRTR 2012). Since 1995, pilot and field-scale soil washing operations with a treatment capacity of 0.2–10 tonnes per hour have been conducted in the United States, Canada, Australia, Korea, and the European Union (USEPA 2013). The short duration and potential cost-effectiveness of soil cleaning. At large scales, the cost in the United States in 2010 varied from \$70 m⁻³ soil to \$183 m⁻³ soil at small scales (FRTR 2012).

c. Solidification

Ex-situ soil solidification involves removing metal-contaminated soil from the site, moving it to a facility for treatment, screening out coarse materials (such as those larger than 5 cm), and combining it with a binder in an extruder. The binders spread throughout the soil, establishing a solid, water-resistant barrier around the impurities. The method is also known as "micro encapsulation." Ex-situ stabilisation is the term for a technique that uses a stabilising agent rather than a binding material to chemically immobilise impurities (FRTR 2012).

Molten bitumen, emulsified asphalt, modified sulphur cement (a thermoplastic polymer melting at 127–149°C), polyethylene, pozzolan cement (fly ash, kiln dust, pumice, or blast furnace slag), and Portland cement are some of the binding materials used for pollutant encapsulation. If soluble phosphate or lime is applied, the substance immobilises the heavy metals in the soil rather than hardening it. The direct encapsulation of contaminated soils in polyethylene or bitumen wraps to create solid waste blocks that may be dumped in a nonhazardous landfill is another possibility. (FRTR 2012) Ex-situ solidification is a tried-and-true method of soil remediation that has been used in more than 200 projects in the United States, with costs ranging from \$120 to \$220 per m³ of soil treated (USEPA 2016a). Although reasonably priced, it is quick and effective. Up to 1000 kg/hr of waste processing rate can be accomplished during scale-up operations. The approach has the substantial downside of increasing waste volume through solidification, which can even double the initial amount of soil that has to be treated. Ex-situ solidification's residual material need extra disposal. The material may be placed on site with frequent inspection in accordance with the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) of the United States.

d. Vitrification

A thermal remediation method called vitrification utilises heat to turn polluted soil into solids that resemble glass. Since 1980, the technology has been developed and put to the test. In actuality, polluted soil receives intense energy application to create a high temperature zone (>1500°C). The area's soil subsequently melts into molten "lava," which cools to form glasslike substance (Meuser 2013). The organic pollutants are eliminated while the heavy metals are contained in the glassy matrix. The resulting vitrification structure is robust, long-lasting, chemically inert, and leach-resistant. There are three main types of vitrification depending on the energy source: thermal vitrification, electrical vitrification, and plasma vitrification. Electrical vitrification involves applying high voltage electricity to graphite electrodes placed at predetermined intervals inside the contamination site to generate heat. Thermal vitrification involves heating a rotary retort containing contaminated soil with an external heat source like microwave radiation or natural gas (high temperature is achieved via electrical discharge-induced gas plasma) (Khan et al. 2004). Overall, vitrification is harmful since the transformed soil is useless for agricultural purposes. Although both in-situ and ex-situ applications are possible, the technology has been used in-situ more frequently than ex-situ (such as with electrical and plasma vitrifications) (e.g., thermal and plasma vitrifications) Ex-situ vitrification is simpler to regulate, but radioactive or dispersive pollutants can lead to dangerous exposure to dust and other fugitive emissions. (Bradl and Xenidis. 2005). Ex-situ vitrification uses a furnace using plasma torches, electric arcs, natural gas burners, or microwave radiation emitters to constantly feed contaminated soil into a revolving container walled with refractory. Horsehead Resources' flame reactor, Babcock and Wilcox's cyclone furnace, and Vortec Corporation's

combustion and melting system are a few examples of ex-situ vitrification reactors. The soil that has been treated fuses into molten slag at temperatures above 1100°C and flows out of the furnace bottom entrance as a 658 glassy solid. The furnace's gaseous effluents are collected and processed further (Bradl and Xenidis 2005). High organic matter (e.g., 7%) and high moisture content soils are not susceptible to vitrification (e.g., 10 percent). It also does not apply to soils that have been severely polluted with combustible or volatile organics. Na⁺ and K⁺, two monovalent alkaline cations, must be present in sufficient amounts in the soil (2-5%). Devitrification does happen from gradual weathering during field storage of the waste, even though the glassy substance from soil vitrification is resilient and robust. Depending on the elemental species, silicate glasses dissolve and then leak between 0.1 and 25 percent of their initial contents over a lengthy period of time (for example, thousands of years) (Meuser. 2013). A tested and readily available technology is vitrification. The method was deemed by the USEPA to be the "best demonstrated available technology" for the disposal of waste containing radioactive and heavy metals (Meegoda et al. 2003). The normal size of an in-situ vitrified space is up to 12 m (length), 12 m (width), and 6 m. (depth). The U.S. Department of Energy has created a transportable vitrification system that consists of an electrical distribution unit, an off-gas treatment unit, and process-control components to facilitate field operations. At both pilot and full sizes, there are now four in-situ vitrification projects in the United States. Existing metal-processing tools can be used for ex-situ vitrification (CPEO 2016). For instance, the HandfordVit Plant is a for-profit facility in Handford, Washington, that uses ex-situ vitrification to handle radioactive waste. According to estimates, vitrification in the United States costs between \$330 and \$425 per tonne of soil treated, with ex-situ operations costing the least (FRTR 2012).

Comment [H18]: Author should provide a summary

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