Asian Journal of Environment & Ecology

Volume 23, Issue 4, Page 61-80, 2024; Article no.AJEE.113569
ISSN: 2456-690X

Technologies for Remediation of Heavy Metals in Environment and Ecosystem: A Critical Overview of Comparison Study

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/AJEE/2024/v23i4540

Open Peer Review History:
This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: https://www.sdiarticle5.com/review-history/113569

Review Article

Received: 22/12/2023
Accepted: 26/02/2024
Published: 04/03/2024

ABSTRACT

Ecosystem contamination is a global issue that is directly related to the advancement of contemporary society. Human health and the natural environment are affected that's why heavy metal contamination of the environment is currently a serious environmental issue that affects the ecosystem. Heavy metal pollution receives special attention because it frequently presents the

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greatest remedial challenges. Certain technologies, usually based on physical, thermal, chemical as well as biological processes have long been used to eliminate heavy metals from polluted environments to a level that is safe and acceptable. The kind and characteristics of the heavy metals, the level of pollution and the combination of contaminants in the environment all have a significant impact on how effective these techniques are. The environment is also at risk from a few conventional technologies. Thus, research and development are needed for effective environmentally friendly methods that are based on natural materials or ecosystems. With a focus on novel approaches to remediation techniques, this review manuscript will give an overview of recent exploration and research, attempts to evaluate the effectiveness of remediation and advancements in decontamination technologies that can be applied to eliminate heavy metals from ecosystems. A summary of the causes, consequences and technologies for cleanup are provided for heavy metals.

Keywords: Environment; ecosystem; heavy metals; remediation; technologies.

1. INTRODUCTION

Heavy metals are considered important environmental pollutants due to their great density and high toxicity even at low concentrations [1-2]. The phrase “heavy metal” typically represents metallic elements with an atomic weight more than that of Iron (Fe) (55.8 g mol^{-1}) or a density greater than 5.0 g cm^{-3} and these metals are naturally found in the environment [1,3]. Nonetheless, several metals with an atomic weight less than that of Fe, for example, Cr and others that are referred to as metalloids such as Selenium (Se) and Arsenic (As) are also frequently considered heavy metals [3-4]. Heavy metals can be involved as micronutrients such as Cu, Ni, Mo, Mn, Zn and Fe but they can also be dangerous to humans, like Hg, Pb, Ni, Cu, Cd and Co depending on the degree of exposure [3,5]. The eight heavy metals recognized by the United States Environmental Protection Agency (USEPA) as the most common in the environment are arsenic (As), chromium (Cr), lead (Pb), zinc (Zn), cadmium (Cd), nickel (Ni), mercury (Hg) and copper (Cu) [2,4]. Class B metals are non-essential (highly toxic) trace elements that include the above-mentioned heavy metals, according to the coordination chemistry of heavy metals [6]. Table 1 lists a wide category for heavy metals along with examples of an ill-defined collection of substances called heavy metals that is mostly found at contaminated locations [7]. Their characteristic is their extended survival in the natural environment, which can have detrimental effects on the health of people, animals, and plants, even at extremely low concentrations like 1.0 or 2.0 µg in certain situations [2,4,8]. When dangerous heavy metals such as Cr, Pb, Hg, Cd and others are disposed of by industry, they do not decompose and contaminate soil and water to a greater degree [9-11]. The high propensity of heavy metals causes them to collect in a variety of environmental matrices, leading to concentrations that are misleadingly greater than the recommended average safety limit [12-15]. The maximum amount of heavy metals that can be present in an aqueous medium is as follows: Cr-0.01 mg/L, Ar-0.01 mg/L, Pb-0.015mg/L, Hg-0.002 mg/L, Cd-0.05 mg/L and Ag-0.05 mg/L, in accordance with the Comprehensive Environmental Response Compensation and Liability Act, USA [2,16-18]. A high concentration of heavy metals can be a major contributing factor to numerous human life-threatening conditions, including cancer, atherosclerosis, Alzheimer's disease, Parkinson's disease, and others [2,19].

To enhance the surrounding and contaminated area's environmental conditions and lower the risk to people and the environment, remediation efforts seek to convert unsuitable property into usable usage and preserve land resources [20]. Activities taken to protect human health and the environment by cleaning up, mitigating, minimizing, correcting, eliminating, controlling, containing, and preventing the release of a contaminant into the environment are referred to as remediation. These cleanup technologies can be applied on-site or off-site, utilizing three types of remediation treatments such as electrical, chemical techniques, and biological [21-23]. The purpose of this article is to accurately describe and assess the most recent technologies used in the literature to remediate heavy metal-affected soils to determine the best technique to use in contaminated soils and to reduce the risks associated with these hazardous metals in Egyptian conditions [2,24].

Table. 1. Heavy metal classification using examples

category of heavy metal	Example	Reference
1.Macro-nutrient elements	Cobalt, Iron	[2,3]
2.Components of micronutrients	Nickel, Molybdenum Chromium, Manganese, Copper	[2,3]
3.Extremely harmful substances	Mercury, Lead, Cadmium, Silver, Tin, Palladium, Bismuth, Arsenic, Zinc, selenium, Gold Platinum.	[2,4]
4. Precious components	Gold, Platinum, Ruthenium, Silver.	[2, 6]
5. Radionuclides	Uranium, Thorium, Radium, Cerium, Praseodymium.	[2,7]

2. POLLUTANTS IN THE ENVIRONMENT: METALS

The earth's crust contains naturally occurring elements known as heavy metals. Both natural and anthropomorphic activities such as smelting, mining, industrial production and the usage of metals and metal-containing compounds for domestic and agricultural purposes, result in heavy metal pollution [2,24]. Numerous researchers have reported that these sources are involved in human exposure and environmental pollution. Heavy metals are known for their toxicological characteristics which include their lengthy half-lives, long residence times in soil (>1,000 years), chronic and sub-lethal effects, teratogenic, bioaccumulation, bio-magnification and carcinogenic properties. [2,25].

2.1 Distribution of Heavy Metals in the Environment

2.1.1 Natural resources

2.1.1.1 Heavy metals in soils

Rocks break down into small particles or soil due to several factors such as temperature, ice and water. Because of the rich and varied binding properties that exist between the soil and heavy metal associations, the soil matrix serves as a significant reservoir or transport medium for heavy metals. [2,25]. Metals bioaccumulate in the environment instead of decomposing like organic contaminants do. The metal ions may be adsorbed, exchanged, reduced, oxidized, catalyzed, or precipitated by the soil matrix. [2,26]. The pH, amount of water present, temperature, distribution of particle size, kind of metal and amount of clay all affect these processes. The mobility, solubility and toxicity of the heavy metals in the soil will be determined by this composition.[26]. Minerals are often dissolved by reacting with water and carbonic acid [2,27]. Fine particles are formed by the dispersion of insoluble materials. Metals and metalloids from gasoline, sludge, animal dung, wastewater irrigation, air deposition and other sources pollute soils [27]. The most common heavy metals detected in soils are Cr, Cd, Zn, Pb and Hg. These metals have an impact on the food chain and reduce agricultural productivity because of bioaccumulation and bio-magnification. [2]. Table 2, provides regulatory guidance and ranges of soil concentrations for several heavy metals.

The rapid creation of heavy metals through man-made cycles, direct exposure of mine samples during transportation from mines to environmental regions with high metal disposal, etc, represent a few of the reasons heavy

Table 2. Heavy metal concentration levels and regulatory guidelines

Metals	Range of soil concentration (mg/kg)	Limits set by regulations (mg/kg)	Reference
1. Pb	1.00-69000.00	600.00	[2, 22]
2. Cd	0.10-345.00	100.00	[2, 22]
3. Cr	0.05-3950.00	100.00	[2, 24]
4. Hg	<0.01-1,800.00	270.00	[2, 25]
5. Zn	150.00-500.00	1500.00	[2, 25]

metals existing in the soil become pollutants. [4,27]. The formula that follows can be used to express the heavy metal balance in the soil.

$$Mtotal=(Ma+Mp+Mip+Mag+Mow+Mf)-(Ml+Mcr) \quad -(1)$$

where "p" denotes the parent material and "M" denotes the heavy metal “a” is the atmospheric deposition, “f ” is the fertilizer sources, “ag” is the agrochemical sources, “ow” is the organic waste sources, “ip” are other inorganic pollutants, “cr” is the crop removal, and “l” is the losses by leaching, volatilization[4,27].

2.1.1.2 Water containing heavy metals

The types of soil, rocks, and water flow all affect the metal content of surface waters such as lakes, ponds and rivers. The path that metals on the soil's surface take is carried away and ends up in reservoirs and sewage [2]. While passing through the atmosphere, rainfall becomes polluted. Water sources are contaminated when several types of industrial waste flow into them [2,27]. Industrial wastes, deep well liquid discharge, landfill leachates etc. all contaminate groundwater. The metal content of the water is also influenced by other factors like temperature, pH, the presence of living things, cation exchange, evaporation and absorption as well as others. This has compelled numerous researchers to create a variety of technical remediation procedures to lower these contamination levels in the Table 3 environment below the regulatory limit.

2.1.1.3 Heavy metals in the atmosphere

Surface erosion and colloid loss release heavy metals into the environment as gasses and particles. Forest fires, volcanic eruptions, mineral dust and sea salt particles are some of the sources of heavy metals in the atmosphere. [2, 27]. In addition to these natural sources, certain industrial activities that create dust such as those in metal smelters and cement plants can also be the cause of heavy metal air pollution. [2,26]. Volatile metals in the atmosphere such as Sb, Hg, As, and Se are carried by gases and particulates. Particulate forms of metals such as Cu, Pb and Zn are transported. [2,27]. The quantity and composition of industrial pollutants, environmental sensitivity, potential for environmental release, proximity of these heavy metals in humans and their impact on health are only a few of the site-specific elements that determine the presence of heavy metals [6].

2.1.1.4. Heavy metal sources that are anthropogenic

Numerous human activities discharge heavy metals into the environment. Surface water absorbs heavy metals through infiltration as a result of the constant use of pesticides and fertilizers for crop production. [6,27]. Phosphate fertilizers frequently contain zinc and copper and their input is closely correlated with the concentration of heavy metals [7-8]. Pesticides used in agriculture contain metals including Hg, As and Pb in addition to Zn and Cd. Despite the discontinuation of metal-based pesticides, heavy metal deposition in a variety of environmental matrices has grown as a result of prior uncontrolled pesticide application [8,27]. Moreover, several industrial processes such as waste disposal, coal combustion, mining and effluent streams have increased the amount of heavy metal contamination in the environment. [2,9] and Fig. 1 provide illustrations of the sources.

Table 3. European Union (EU) and Indian guidelines for heavy metals in food, drink and soil

heavyweight metal	Soil (μg/kg)	Food (mg/kg)	Water (mg/L)	soils to EU requirements (μg/g)	Reference
Cr	-	20.00	0.05	150.0	[2]
Cd	3.0-6.0	1.50	0.01	3.00	[2,11]
Cu	135.0-270.0	30.00	0.05	140.0	[2]
Fe	-	-	0.03	-	[2, 11]
Ni	75.0-150.0	1.50	-	75.00	[2]
Pb	250.0-500.0	2.50	0.10	300.0	[2]
Zn	300.0-600.0	50.00	5.00	300.0	[2, 12]
As	-	1.10	0.05	-	[2]
Mn	-	-	0.10	-	[2, 12]

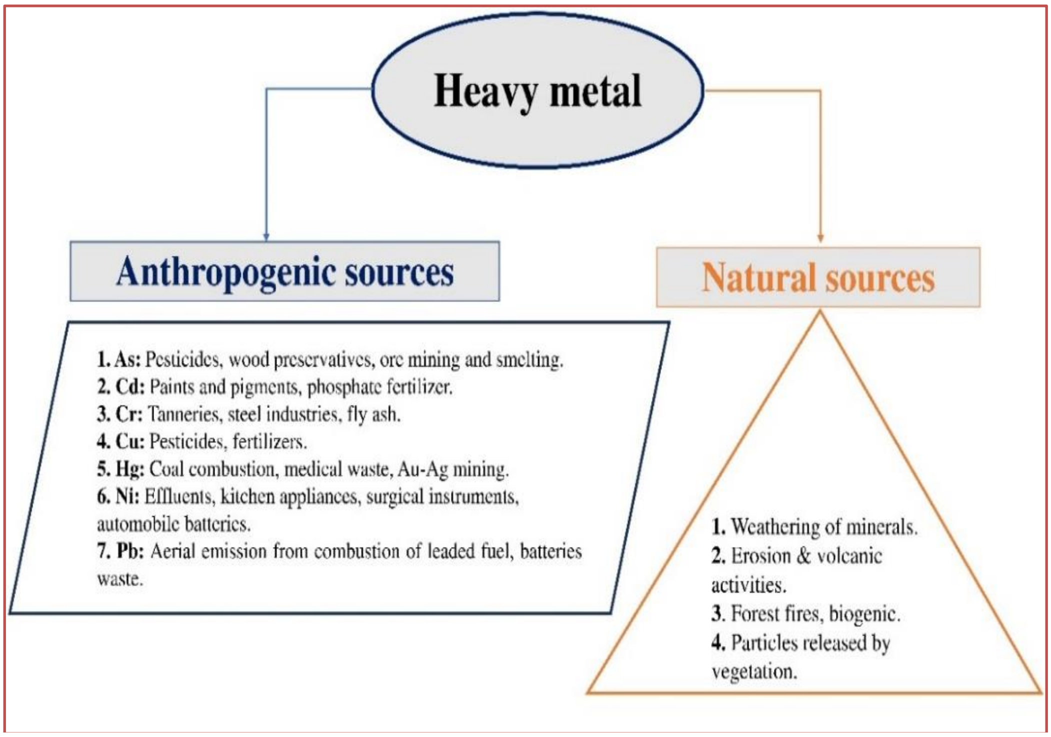

Fig. 1. Anthropogenic and natural sources of heavy metal

2.2 Effects of Heavy Metals in Environment

Because they are poisonous, do not biodegrade in the environment and readily accumulate in living things, heavy metals are significant environmental pollutants. Humans, animals and plants are all impacted by the direct or indirect discharge of heavy metals into the environment from a variety of sources [8,27]. It has also been observed that this heavy metal pollution in soil disrupts the food chain, lowers food quality because of Phytotoxicity, depletes soil fertility and has other effects on the ecosystem [27]. Ingestion, skin contact, and inhalation are all of the basic ways that one can become exposed. There are major health risks and environmental degradation associated with the increasing risk of human exposure to heavy metals. Consequently, these metals are referred to as systemic toxicants that can cause the conditions listed in Table 4 in humans, which include diseases of the heart, abnormalities in development, neurological and behavioural disorders, diabetes, hearing loss, hematologic and immunologic disorders and various types of cancer. [9,28].

Table 4. lists a few of their harmful health impacts along with how they're applied

Element	Uses	Adverse health effects	Reference
Cd	vehicle exhaust	impact on the heart, kidneys, and respiratory system.	[2, 8]
Cr	Pesticides, detergent.	Mental disturbance, cancer, ulcer and hyperkeratosis.	[2, 8]
Cu	Most uses are based on electrical conductor properties.	Through interactions with other nutrients, anemia and other harmful consequences are indirectly caused.	[2]
Pb	Batteries, alloys.	Neurotoxic.	[2, 9]
Ni	Batteries, Catalysts, Electronics.	allergies to the skin, lung fibrosis and cardiovascular disorders	[2, 9]
Zn	Fertilizers, plastics, pigments.	stomach discomfort, headache, irritability, lethargy, nausea, vomiting, diarrhoea and anemias.	[2]

3. REMEDIATION TECHNOLOGIES

3.1 Selection Criteria for Remediation Techniques

The primary consideration while choosing acceptable technology is which technology is best suitable for the task at hand. Many approaches are proposed for remediating soil and groundwater, ranging from sophisticated biological processes to highly technical advanced engineering technologies [1,28]. The methods might be unique to the contaminant or classes of contaminants present at the site. Remedial technologies need to align with the principles of minimal energy and resource use, reduced waste generation, and reduced environmental impact to align with the notion of sustainable development. Stated differently, the technologies must possess unique features [1,29]. Short- or long-term efficacy in achieving remediation goals, efficacy of pollutant reduction in site, decrease in contaminant toxicity and remediation cost-effectiveness are some of the decisive factors for screening remediation procedures [1,29].

3.2 Categorization of Remedial Technology

3.2.1 Based on type of application

There are two types of remediation technologies: on-site and off-site technologies and in-situ and ex-situ remediation methods. [9,28] expressed in Table 5. In situ or ex-situ techniques are used to carry out on-site remediation on the contaminated site. Contaminated soil or groundwater is extracted from the excavated site and treated off-site (ex-situ approach). [2,28]. It requires that the polluted groundwater or soil be transported to the treatment facilities. A contaminated material in soil or groundwater is treated in the location where the contamination is identified using an in-situ approach. After the cleanup procedure, generally, undisturbed unexcavated soil or unextracted groundwater can be treated using in-situ technology [29]. The in-situ remediation method requires complete information on the geological, hydrogeological, and other features of the contaminated area in addition to the physical, chemical, and biological properties of the pollution. In-situ remediation is less inconvenient to the site, more cost-effective, and improves worker safety during the treatment process. Excavated soil or extracted groundwater is treated using ex-situ technology. Ex-situ treatment can be provided both on and off-site [1,2]. The following technologies for in-situ and ex-situ remediation have been used to reduce the levels of contaminants such as heavy metals.

3.2.2 Technologies appropriate to the required processes

Technologies such as biological, physical, chemical and thermal separation are dependent on the procedures that are used. Microbiological metabolism can be used in bioremediation processes to transform or degrade soil or groundwater into harmless substances. The latter can include water, fatty acids, carbon dioxide and other substances. To chemically convert, segregate or contain the contamination, physical and chemical treatment technologies require the physical or chemical properties of the pollutants as well as the contaminated media [11-13].

In the physical separation process, metal contaminants are phase transferred out of the contaminated media by taking advantage of variations in specific physical qualities such as size, density and magnetic and hydrophobic surface features, between metal-bearing and soil particles [12-15]. In the mining and mineral processing industries, physical separation is a method of concentration used on metal-bearing particles; however, in soil remediation, it refers to the removal of metal particles from the soil. The exact sorption capacity of heavy metal chemical forms in soil, their concentration level and soil features all influence the use of physical separation techniques [1,29]. Because of this, these technologies are mostly employed in industrial areas that are influenced by humans and have significant levels of heavy metal concentrations in anthropogenic soils [13,30]. Excavation of soil and subsequently separation of the particles according to their physical characteristics are indications of ex-situ technology. These techniques are suitable for use in two situations [1]. when the contaminant is concentrated in particular fractions of particle size, as is often the case with trace elements in the fine fraction of soil and another when the contaminant is present in the soil as discrete particles [1,13-14]. Fig. 2. summarizes the heavy metal remediation technologies' classification.

Table 5. Classification of remediation

Classification of Remediation		
a) Technology both in-situ and ex-situ	b) technologies that are in- situ	c) ex-situ technologies
separation/concentration, stabilization/solidification, and bioremediation [11].	soil additions, chemical treatment, electrokinetics, barriers/treatment walls, and phytoremediation [11].	soil washing [11].

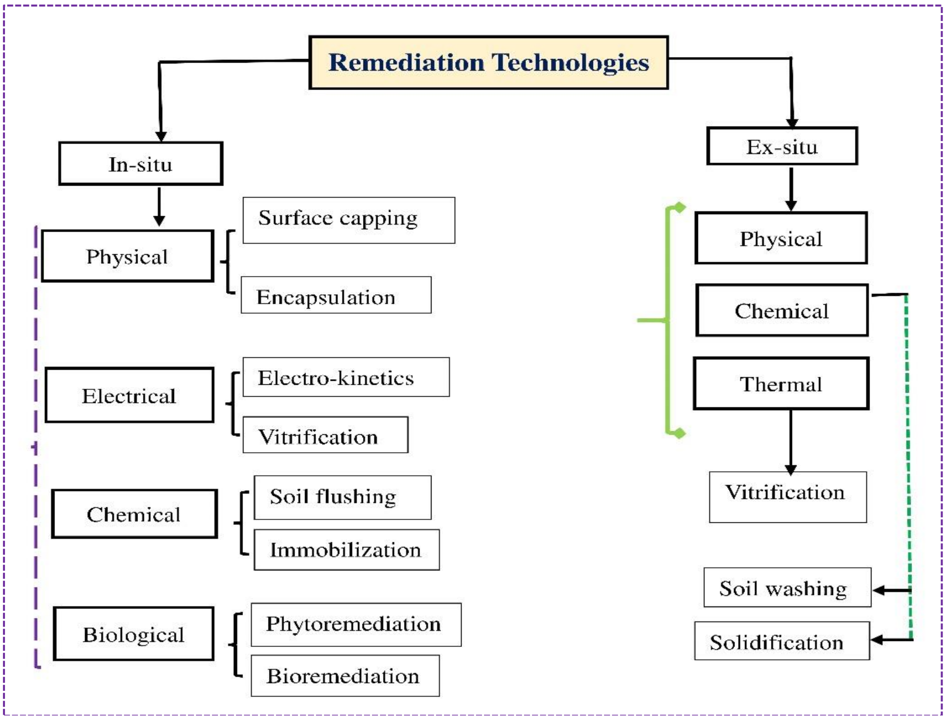

Fig. 2. Classification of remediation technologies

Thermal processes involve the use of heat to cause contamination in many ways, including burning, decomposition, destruction and volatility. Because the results of the verification process are similar, some classifications include the vitrification in the S/S (stabilization/solidification) sub-category [14]. On the other hand, the procedure differs from the traditional S/S technique. Electrodes that can conduct electricity and harden as the soil cools are inserted into the soil to perform vitrification. Electrical power is used in in-situ verification to melt and heat contaminated soil [11,30]. Organic pollutants are eliminated by pyrolysis, however off-gas treatment is necessary because volatile metals may develop in the waste. Heavy metal-contaminated soils, organic contaminants with high sorption coefficients and radioactive materials can all be treated by vitrification [14]. But in soils that include a lot of organic matter, a lot of moisture, or big metallic objects like pipes or drums, the efficacy is diminished. Alternatively, in-situ soil heating, which can be accomplished via radiofrequency or power line frequency heating, decontaminates soils through vaporization, steam distillation and stripping [14]. Toxic gasses may also be generated during the vitrification process. For soils contaminated with As, Pb and Cr there is a full-scale application. Vitrification is another method for treating mixed wastes. The efficiency of a big-volume process can be impacted by high clay, moisture and debris concentrations [14,30].

3.3 Heavy Metal Remediation Using Modern Technology

There are four categories of modern heavy metal remediation technologies: chemical remediation, electrokinetic remediation, phytoremediation and bioremediation.

3.3.1 Electro-kinetic remediation

By passing a low-voltage direct current (DC) to electrodes buried in the soil, an electrical field is produced in the soil matrix during the in-situ electro-kinetic (EK) remediation process [15]. Applying this electric field may cause heavy metal pollutants to be mobilized, concentrated at the electrodes and removed from the soil [15]. A field setup for electro-kinetic remediation is built, complete with a well, electrolyte filling, cathode (-) and anode (+) insertion, electric field applied, electro-osmosis and electrolysis of water, metal ion desorption via acidic front, electro-migration and precipitation or dissolution of metal ions and pumping and storing of used electrolytes [15,29] in Fig. 3.

It is possible to arrange the electrodes in a horizontal or vertical array. An electrical field forms between the anodes and cathodes when DC is delivered to the electrodes. The application of an electric field has several impacts on pollutants, water and soil [16,30]. These consequences consist of electrophoresis, electromigration, electroosmosis and changes to the system's pH [17,31]. The term electro-migration describes the movement of anions and cations caused by an electrical field. These ions gather in the solutions close to the electrodes or they could react there and plate metal onto the electrodes or release gaseous substances [17, 30]. The movement of ions containing liquid about a stationary charged surface or the bulk transport of water through the soil caused by an applied electrical field is known as electro-osmosis. Because of the electrolysis processes at the electrodes, pH changes happen when electricity is applied. Water is oxidized at the anode, producing hydrogen (H+) ions. These ions create an acid front and migrate to the cathode [17].

A charged particle moving through a liquid due to an electric field is called electrophoresis. As a base front moves towards the anode, hydroxyl (OH-) ions produced by the reduction of water at the cathode as shown in equation 3, migrate in contrast [17].

$$2H_2O - 4e^- \longrightarrow O_2 + 4H^+ \qquad \text{(Equation 2)}$$

$$4H_2O + 4e^- \longrightarrow 2H_2 + 4OH^- \qquad \text{(Equation 3)}$$

Approximately twice as quickly as OH- ions are transported, according to [16]. Because of this, the acid front advances faster than the base front [18,31]. The soil between the electrodes will become acidic unless the soil buffering capacity slows down the proton (H+) ion transport. Because of the desorption and dissolution of soil species, this acidity causes pollutants to become more soluble [18]. When pollutants are present in the soil pore fluid in an ionic state, they are extracted from the soil at the electrodes by migrating to the electrode that is opposite in polarity under the applied electric field or by electro-osmosis. The pollutants can be extracted and removed via electro-deposition, precipitation or co-precipitation at the electrode [18,31]. Numerous subsurface factors, including soil type and particle size, contaminant concentration,

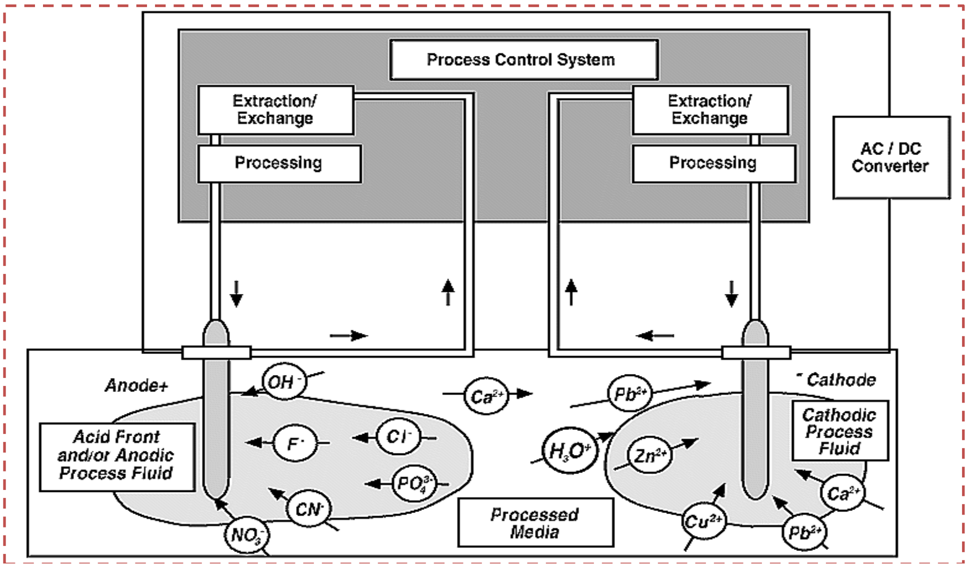

Fig. 3. A Flow diagram of the electro-kinetic remediation process

ionic mobility, total ionic concentration, types of contaminated species and their solubility etc., affect the heavy metal extraction rate and efficiency of EK remediation. The application of EK remediation may encounter additional difficulties if organic pollutants and soil organic matter are present [15].

The advantages and disadvantages of electro-kinetic remediation are illustrated in Table 6.

3.3.2 Chemical remediation

Chemical processes involve the reduction of pollutants' bioavailability and mobility as well as the reactivity of certain chemicals with heavy metals. The foundation of heavy metal remediation technologies is organic-metal complexion reactions, oxidation-reduction and precipitation all well-known and well-researched chemistry processes found in fields such as chemical technology, environmental chemistry, analytical chemistry and radio-analytical chemistry [31]. One disadvantage of using chemical procedures is that there may be unintended environmental repercussions. This must be considered while selecting chemical reagents for treatment processes. Different insoluble compounds can precipitate out of the solution containing dissolved heavy metals in groundwater [1,31]. The most frequent precipitates of heavy metals are phosphates, carbonates, sulfides, hydroxides, oxalates and a few other forms. The insoluble compound's solubility product constant (Ksp), characterizes the precipitation reaction's perfection. Heavy metals like Cu, Cd, Pb and Zn; and phosphate-containing precipitating reagents U, Pu are used to convert them into a low-solubility phosphate mineral phase that is not bioavailable [1,31]. The extremely low Ksp values enable effectiveness. For instance, the solubility product constants of Pb apatite (pyromorphite) and U-phosphate (autunite) are Ksp=10.0 – 80.0 and Ksp=10.0 - 49.0, respectively [19]. The precipitated substance is more insoluble the lower its solubility product constant. When insoluble materials precipitate, two additional processes, such as co-precipitation and sorption, happen simultaneously with the precipitate's creation [30]. As a result, heavy metals that exist in small and micro concentrations in aqueous media also concentrate in the solid phase. Contaminants enter the solid phase by spontaneous processes such as precipitation, co-precipitation and sorption which have a propensity toward reduced disorder [1]. Metal contaminants can be detoxified or have their mobility reduced through chemical treatment using both oxidative and reductive methods Σ19γ. This technique is frequently used for the treatment of wastewater [20,31]. Hypochlorite or chlorine gas, hydrogen peroxide, and potassium permanganate are added to oxidation reactions that detoxify, precipitate or solubilize metals. Acidic or basic soils can have their pH adjusted by neutralization processes. When alkali metals like sodium, sulfur dioxide, sulphite salts and ferrous sulphate are added, reduction processes begin to occur [21]. Pretreating the soil chemically can be done sometimes to prepare it for further treatments or solidification. For instance, during solidification/stabilization (S/S), chemical reduction of Cr (VI) is carried out. With S/S, oxidation is less frequently utilized. However, these reactions are not specific, and other metals may be changed into more mobile or risky forms as a result. As arsenic (V) is less dangerous than arsenic (III), it is most suitable for chemical oxidation [22]. While low concentrations of As (V) co-precipitate with Fe $(OH)_2$ with high concentrations of Fe (III) to create arsenic ferrihydrite, a product resistant to acid and neutral leaching, high concentrations of As (V) and Fe (III) co-precipitate to form $FeAsO_4$. Additionally appropriate for reduction are silver, mercury, lead, and selenium. Although injecting these chemical treatments into the groundwater can be done in situ, there is a chance that more contamination will be introduced [21,32]. The majority of the metals can be removed, and application is quick and simple. covers a wide range of inorganic contaminants and is quite inexpensive [15]. However, there are disadvantages such as large sludge production and disposal problems. Both long-term monitoring and permanent solutions are necessary. There's a chance it might cause further pollution [15].

3.3.3 Bioremediation techniques

Biological solutions for remediation utilize the protective mechanisms that microorganisms have evolved against metals and oil products. Oxidation, reduction, sorption, and methylation are examples of common protective processes [32]. Currently, biotechnologies utilizing these mechanisms are being developed to a high degree for the remediation of organic substances; however, there is minimal experience with inorganic pollutants. [15-17] are explained in Table 7.

Table 6. Advantages and disadvantages of electro-kinetic remediation

Causes	Description
Advantages	passive and in-situ methodology. Low-cost and powered by solar. less soil erosion and less contamination and dust spreading through the soil. Plants are easily harvested [15].
Disadvantages	Few practical experiences make many regulatory bodies reject it. There is still much to learn about the toxicity and bioavailability of breakdown products. Compared to conventional physico-chemical procedures, the treatment is slower. Animal consumption of accumulator plants can result in the spread of contamination throughout the food chain. The decontaminated area needs to be sufficiently large to accommodate the use of cultivation techniques [15].

Table 7. Advantages and disadvantages of bioremediation techniques

Advantages	Disadvantages
The process of bioremediation takes advantage of microorganisms' natural capacity to remove contaminants of water, soil, and sediment by using solar energy as energy. Compared to other physiochemical treatment techniques, this technique is less costly. It requires less energy than other technologies. Little to no treatment residue is often found [15].	Bioremediation is a slow process. In general, treatment times are considerably longer compared to the results of other remediation techniques. Not all of the pollutants have been removed from the contaminated site. Inorganic pollutants cannot be treated by bioremediation. The site requires soil for in-situ remediation. [15].

Table 8. Mechanisms of phytoremediation

Types	Mechanisms
I. Rhizosphere biodegradation	During this process, the plant releases naturally occurring substances through its roots, giving soil microorganisms nutrients. Microorganisms accelerate biological deterioration [23].
II. Phyto-stabilization	Instead of degrading pollutants, the plant produces chemical compounds that immobilize them [23].
III. Phyto-accumulation also called phytoextraction	Along with other nutrients and water, the pollutants are absorbed by the roots of plants. Instead of being eliminated, the polluting material becomes incorporated into the plant's leaves and branches. This process is primarily applied to metal-containing wastes. [23].
IV. Hydroponic Systems for Treating Water Streams (Rhizofiltration)	Similar to phyto-accumulation, rhizofiltration involves growing plants in greenhouses with their roots submerged in water. Groundwater treatment in ex-situ is possible with this technology. To irrigate these plants, groundwater is forced to the surface. Sand combined with vermiculite or perlite is an example of an artificial soil material used in hydroponic systems. The roots are removed and thrown away as soon as they are saturated with pollutants [23].
V. Phyto-volatilization	Organic pollutants are absorbed by plants and then released into the atmosphere through their leaves [23].
VI. Phyto-degradation	Pollutants are broken down and eliminated by plants within their tissues. [23].
VII. Hydraulic Control	By regulating the flow of groundwater, trees provide indirect remediation. Because their roots grow deeply into the ground and create a dense mass that can absorb significant amounts of water, trees function as natural pumps. A poplar tree may collect up to 30.00 gallons of water daily from the ground, whereas cottonwood trees can absorb up to 350.00 gallons daily [23].

3.3.4 Phytoremediation

Using a variety of plant species, phytoremediation is a bioremediation technique that removes, transfers, stabilizes, or removes pollutants from soil and groundwater. There are numerous varieties of mechanisms for phytoremediation in Table 8. [23].

The primary benefits include in-situ and ex-situ; compatibility with a wide range of organic and inorganic compounds; suitability for large-scale soil remediation; economical relative to traditional methods; ease of implementation and public acceptance; preservation of natural resources; and environmental friendliness [15,32]. Another way to take it is that the remediation of a contaminated site takes years, is slower than traditional procedures, less effective at locations with high concentrations of contaminants, and is unknown how harmful and bioavailable the products of biodegradation are. The removal of pollutants stored in plants following harvesting is ineffective in the winter and causes pollution again [15,33]. Because it's so costly, the aforementioned technologies without bioremediation are seen as ineffective. It is now the most practical technique for heavy metal remediation.

3.4 Bioremediation Method

The ability of specific biomolecules or biomass types to bind and concentrate particular ions or other compounds present in aqueous solutions is known as bioremediation. Microorganism-based bioremediation has a lot of potential for growth in the future because it is environmentally friendly and may be economical. [24]. Numerous microorganisms, such as yeasts, fungus, bacteria, and algae, can function as biologically active methylators to alter or at least reduce dangerous species. [25,34]. High local concentrations of metals can occasionally arise via the efflux or exclusion of metal ions from cells, which is a key step in many microbial detoxification processes. Here, the metals might combine with biogenic ligands and precipitate [26]. Although microorganisms can't destroy metals, they can change their chemical composition through a surprising number of different mechanisms [24,5]. Bioremediation is the process by which highly harmful compounds are transformed into less toxic chemicals with the use of microorganisms, usually one type of organism or a group of them. The technology, which uses microbes' metabolic potential to clean up contaminated surroundings, has been suggested as a viable alternative because it is more cost-effective and efficient than other physicochemical techniques. Microorganisms can break down poisonous chemicals into less dangerous metabolites or into harmless end products [35]. Because they can use pollutants as possible sources of energy through metabolism, microorganisms can also thrive in contaminated environments [24]. Chromium, copper, cadmium, and lead collectively account for 70.0% of applications of metals used in bioremediation procedures utilizing microorganisms, however nickel and zinc are also utilized. [27,36]. Mercury and arsenic are some additional metals that are utilized less frequently [37,38].

3.5 Types of Micro-organisms Used in Bioremediation

Numerous organisms, including eukaryotes and prokaryotes, can naturally biosorb harmful heavy metal ions, as demonstrated by numerous studies. The following are a few instances of microorganisms that have been researched and deliberately employed in heavy metal bioremediation treatments: Table 9 [27,39]. The capacity of some yeasts such as *S. cerevisiae* and other fungus, including Aspergillus and Penicillium to remove heavy metals from specific environments has been shown in recent studies. Water bodies have been utilized to remove heavy metals using the species *Bacillus subtilis, Staphylococcus aureus* and *Escherichia coli* in Table 9 [24,40].

4. CHEMISTRY OF MICRO-ORGANISM

A variety of macromolecules, including polysaccharides and proteins with a high concentration of charged functional groups such as carboxyl, imidazole, sulfhydryl, thioether, phenol, carbonyl, amide, ester sulfate, amino and hydroxyl groups are found in the structure of a microorganism's cell wall [3]. Adsorption takes place when the solution's positively charged metal gravitates toward these functional groups [37,40]. Microorganisms' adsorption ability can be increased by taking advantage of how they are cultivated which can have an impact on the composition of their cell walls. By using functional groups found in their cell walls, such as ketones, aldehydes, and carboxyl groups, bacteria can extract heavy metals from wastewater and reduce the amount of chemical sludge that results. [37]. Metals are taken up by both gram-positive and gram-negative bacteria. Algae: Red, brown, and green are also employed as biosorbents. Certain functional components found in bacteria, including alginic acid, xylans, galactans and uronic acid containing carboxyl and sulfate groups, can exchange ions. Algae are advantageous as biosorbents because, in contrast to other microbes like bacteria or fungi, they often do not create poisonous chemicals. [3].

In addition, yeasts and fungi are employed for the adsorption [3,40]. The largest benefit of fungi is their extreme variability; they can range in size from tiny moulds to mushrooms. They yield a significant biomass and are simple to grow. Polysaccharides and glycoproteins, such as amine, imidazole, phosphate, sulfate, sulfhydryl, and hydroxyl groups are abundant in the cell walls of fungi. [37]. On the other hand, yeasts have micro-fibrillar structures in their cell walls that are made up of more than 90.0 % polysaccharides. In these walls, the primary groups are hydroxide, carboxyl, amine, sulfate and phosphate groups [3,41].

4.1 Mechanisms Associated with Bioremediation by Micro-organisms

Bio-sorption and bio-accumulation are the two subcategories of bioremediation. Whether a microbe is prokaryotic or eukaryotic influences how it interacts with heavy metal ions; prokaryotes are less vulnerable to metal toxicity than eukaryotes [3,28]. The active extrusion of metal, intracellular chelation (in eukaryotes) by different metal-binding peptides, and conversion into other chemical species with decreased toxicity are the potential interaction mechanisms [28]. Microorganisms must attack the contaminants enzymatically and transform them into innocuous compounds for bioremediation to be effective. Higher species such as bacteria, have evolved defence mechanisms against harmful metals that make them harmless [28, 42]. The enzymatic degradation process involves a variety of microbes, including fungi, aerobes, and anaerobes. The majority of bioremediation systems operate in aerobic environments, although anaerobic environments allow microbial organisms to break down compounds that would otherwise be resistant [3,28]. Fig. 4. shows the main categories of microorganisms, such as bacteria, fungus, yeast, and microalgae, that are frequently utilized for the bioremediation of metals.

Bio sorption can occur from both living and dead biomass because it doesn't depend on cell metabolism. On the other hand, passive absorption has a limited and poorly defined function in bioaccumulation, which encompasses both intracellular and extracellular processes. Thus, living biomass is limited to bioaccumulation [29].

4.2 Mechanism of Bio-accumulation

Bioaccumulation is the term for the process of metal accumulation on the cell surface that depends on the metabolic activities of the microorganism as well as the properties of the cell surface [29]. The technique by which the metal attaches itself to a particular location in the biomass is crucial to the effectiveness of the bioremediation technique [3,43]. For example, the free metal ions in sediment pore waters are

Table 9. Shows the capacity of common microorganisms (fungi, bacteria, algae and yeasts) to remove heavy metals from particular environments

Microorganism	Type	Metal	Reference
Algae	Chlorella pyrendoidosa, Ascophyllum nodosu. Spirullina species and Spirogyra species.	U. Cr, Cu, Fe, Mn, Zn, Pb, Cu, Cd and Zn.	[26]
Bacteria	A pseudomonas veroni. ginsengisoli, Sporosarcina.	Zn, Cu, Cd. As	[26]
Fungi	Penicillium, Rhizopus, Aspergillus, and Mucor. Penicillium simplicissimum, Aspergillus niger, and Aspergillus foetidus.	Cu, Fe and Cd. Co, Ni, Mo, V, Fe, Mn, W and Zn.	[26]
Yeast	Candida tropicalis. Saccharomyces cerevisiae	Cr, Ni, Cu, Zn, Cd, Cr and Cu.	[26]

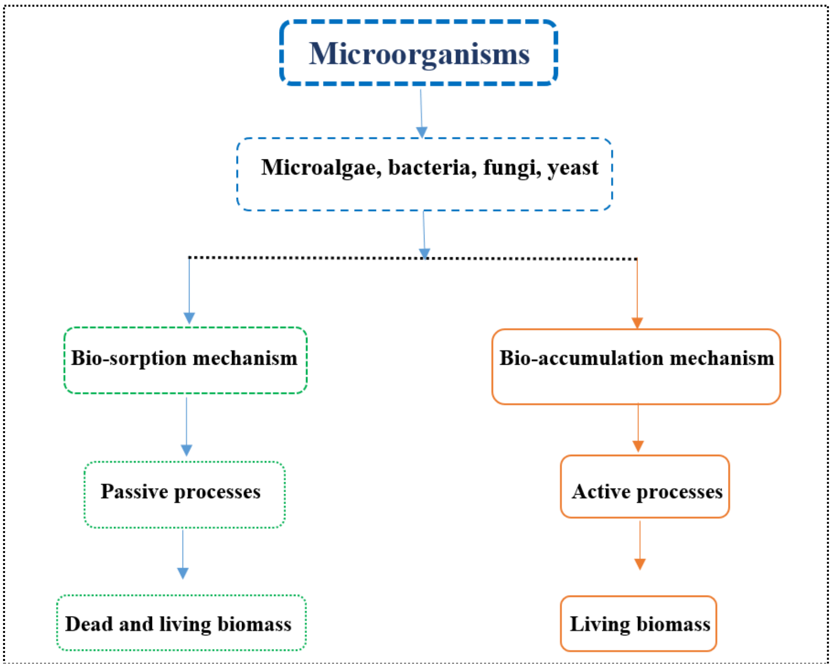

Fig. 4. Microorganisms used in bioremediation and the techniques and processes applied to both living and dead biomass

typically thought to be the most accessible form of metals, yet ingesting sediments is thought to be the primary method of exposure to metals for microorganisms. Thus, microbes' eating habits have an impact on metal accumulation. To prevent potentially harmful effects, a process of metal excretion and/or detoxification starts after heavy metal consumption. On the other hand, if bacteria are kept in detoxified forms, they won't experience the harmful consequences of metal presence [30,43]. Moreover, the type of metal that may attach to ligands that contain oxygen, sulfur, or nitrogen determines how the metal interacts with the biomass. Even though this may only be a basic synopsis of the mechanisms at play, it can serve as a foundation for fresh ideas regarding how to improve the effectiveness of metal uptake by microorganisms [44]. Alternatively, microbes can produce metal-binding proteins such MTs or PCs, which are closely linked to the ability of metal adsorption, accumulation, and resistance [3,30]. One significant subset of these proteins, known as metalloproteins, is involved in controlling the amount of metals present in cells. Outside the cell membrane, metal binding proteins draw metal ions from the solution and help move them to the cytosol, where metallochaperones—specialized protein chelators—transfer the metals to the right receptor protein [3,30]. By applying genetic approaches, the binding sites of the metal binding proteins have been improved to other proteins, such as heterologous metalloproteins. One unique method to increase the adsorption capacity is to use recombinant DNA to change the proteins on the cell surface into heterogeneous ones. For this reason, research has been done on both bacteria and yeasts [23, 30].

4.3 Mechanism of Bio-sorption

Bio-sorption is a fast and reversible passive adsorption process. Physical-chemical interactions between the metal and the functional groups on the cell surface, such as ion exchange, adsorption, complexion, precipitation, and crystallization, are used to keep the metals in place. The biosorption of metals can be influenced by several variables, including temperature, particle size, biomass concentration, ionic strength, pH and the presence of other ions in the solution [3,30] in Fig. 5.

Metals can be retained by microorganisms; therefore, it's important to identify and comprehend the functional groups causing the adsorption phenomena [30]. The passive process of bio-sorption by dead biomass, certain compounds, or their active groups is mostly

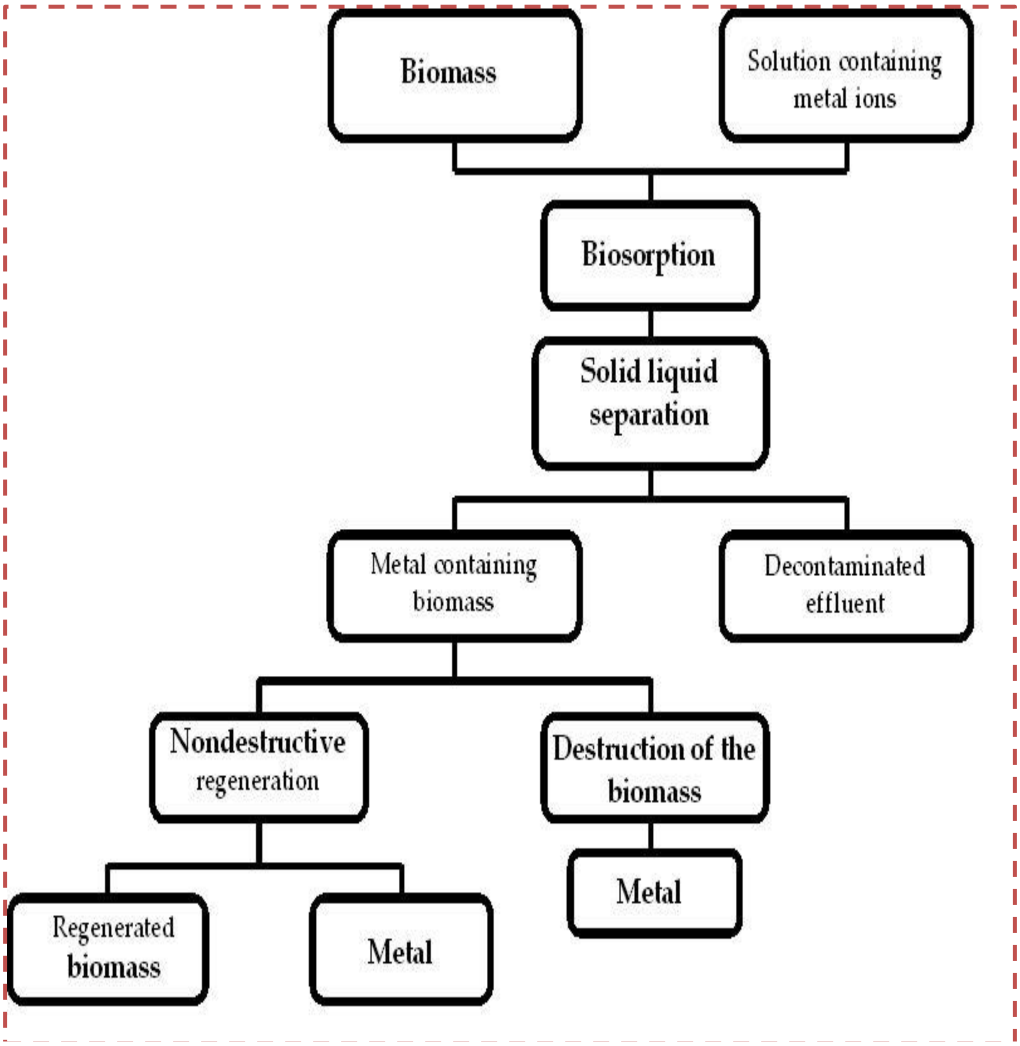

Fig. 5. Schematic diagram of bio-sorption process

dependent on the affinity between the sorbate and the biosorbent. In this instance, chemical sites found in the biomass naturally sequester the metal [30,45]. This process's primary steps are depicted in the figure in Fig. 5. Most of the time, the bio sorption process proceeds quickly and at room temperature and pressure. Following phase separation, an effluent devoid of contaminants and biomass "charged" with metal ions are produced.

[30,46]. The removal of other metal species from other contaminated effluents using biomass makes this technique the most appealing. The alternative, which provides no chance of reuse, is to destroy the biomass [30,47]. Since it clarifies many of the findings from heavy metal uptake tests, ion exchange is a crucial idea in biosorption [30]. The precise process of chemical binding, such as ionic and covalent bonds, should be understood to be electrostatic or London-van der Waals forces, as the term "ion exchange" in this context does not specifically describe the mechanism of heavy metal binding to biomass [30]. An ion exchange process for a biosorbent material is schematically shown in Fig. 6, where Me stands for a metal with valence +2.

The recovery of the metal is a crucial concern following the biomass-mediated extraction of metal from aqueous solutions. A metal desorption technique can do this explained in Table 10 [30,48].

Different types of comparison of technologies are compensated in Table 11 to Table 13. The metals are employed in different perspectives [53-56] such as the crystalline [57-61] and another prominent field [62-63].

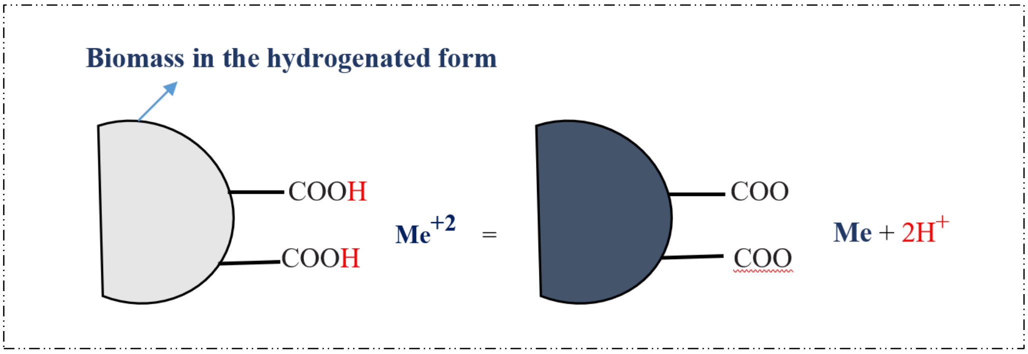

Fig. 6. Schematic diagram of an ion exchange mechanism

Table 10. Comparison between Bio-sorption and Bio-accumulation

Characteristics	Bio-sorption	Bioaccumulation	Reference
Cost	Industrial waste can be used to create biomass. The cost is associated mostly with the transportation and production of biosorbents.	Usually, high. The process occurs in the presence of living cells that have to be preferred.	[34]
pH	Heavy metal sorption capacity is severely influenced by the pH of the solution. Despite this, a broad pH range can support the process.	Significant changes in pH can strongly affect living cells.	[34,49]
Selectivity	Poor. However, this can be increased by modification/biomass transformation.	Better than in the case of bio-sorption.	[34]
Rate of removal	The majority of mechanisms happen quickly.	slower rate due to the longer duration of intercellular accumulation than in the case of bio sorption.	[34]
Regeneration and reuse	Bio sorbents have numerous cycles of regeneration and reuse.	Reuse is limited due to intercellular accumulation.	[34]
Recovery of metals	Heavy metal recovery is feasible with the right eluent.	Biomass cannot be used for any other purpose, not even if it were possible.	[34]
Energy demand	Typically, quite low.	Cell growth requires energy.	[34]

Table 11. Comparison between bioremediation and phytoremediation process

Bioremediation	Phytoremediation
Use of naturally occurring deliberately introduced micro-organisms to consume and break down environmental pollutants to clean a polluted site. Method of removing contaminants from ecosystems and used mainly for organic pollutants. Mainly use microbes. Can be either in-situ or ex-situ. More ecologically friendly. [32, 50].	A process of decontaminating soil or water by using plants and trees to absorb or break down pollutants. A type of bioremediation and amenable to a variety of organic and inorganic compounds. Depends on plants. Mainly an in-situ process. Cost-friendly. [32, 50].

Table 12. Comparison between bio-remediation and chemical remediation

Bioremediation method	Chemical remediation method
It is a cost-effective method compared to other physiochemical treatment methods. Bioremediation is not a utility for the treatment of inorganic contaminants. Often little to no residual treatment. More ecologically friendly [32].	It is a costly method. Covers a broad spectrum of inorganic pollutants. Large amounts of sludge are produced. It has the potential to introduce further contamination [32].

Table 13. Comparison between bioremediation and electro-kinetic remediation method

Bioremediation method	Electro-kinetic remediation method
In-situ and ex-situ. Both active and passive techniques. Fast process. It is eco-friendly. Pollutants can be determined. It can be applied anywhere. High acceptance by the public. [33, 51].	In-situ. Passive technique. Compared to conventional physico-chemical procedures, the treatment is slower. Contamination can move up the food chain. Most of the breakdown products' toxicity and bioavailability are still unknown. The decontaminated area needs to be big enough to use cultivation methods. few years of experience which makes many regulatory bodies reject it [33, 52].

5. CONCLUSION

Effective cleanup techniques are required because heavy metal pollution of the environment is a global issue. For polluted sites to be effectively cleaned up, a variety of remediation approaches are employed. We evaluated the efficacy of many remediation strategies that are frequently employed to clean up contaminated sites in this review. Heavy metal cleanup is now an intricate and challenging task due to the associated costs and technical challenges. Most conventional remediation techniques are ineffective for cleaning up sites polluted with heavy metals. Although physically remediating polluted soil can remove heavy metals completely, these approaches are expensive and disruptive. These techniques are limited to tiny soil areas. Chemical cleanup techniques are quick, easy to use, widely accepted and reasonably priced. But because they can't discharge more pollutants into the environment, these cleanup techniques aren't environmentally benign. Large-scale heavy metal cleanup is made possible by bioremediation, a safe, least harmful, environmentally friendly and economical remediation method. However, more basic and field-based research is still required in this area. The growth environment, plant tolerance to metals and soil solubility of metals all affect how effective phytoremediation is. Although phytoextraction takes longer, it works well for low-to-moderate concentrations of heavy metals. It is possible to combine bioremediation with several other conventional remediation methods to good effect. Plants benefit from the protection that soil microbial interaction provides from heavy metal toxicity and increased absorption of metals through the production of different compounds. Because bioremediation often works with heterogeneous and multiphasic environments, like soils, it requires an interdisciplinary approach incorporating the work of soil chemists, plant biologists, geneticists, microbiologists, and environmental engineers. The results of the study indicate that the primary determinants of the suitability and choice of remediation methods are the associated expenses, the duration needed, the efficacy over an extended period, the degree of widespread acceptance and the site's high and multi-metal contamination.

ACKNOWLEDGEMENT

I want to express my sincere gratitude to the Chairman of the Department of Applied Chemistry and Chemical Engineering (ACCE), Islamic University (IU), Kushitia-7003, Bangladesh, for his advice and friendly behaviour during my project is a tremendous honour and pleasure.

COMPETING INTERESTS

Authors have declared that they have no known competing financial interests or non-financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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