

Integrated remediation techniques for heavy metal pollution in environment

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Abstract: Addressing heavy metal pollution is one of the hot areas of environmental research. Despite natural existence, various anthropogenic sources have contributed to an unusually high concentration of heavy metals in the environment. They are characterized by their long persistence in natural environment leading to serious health consequences in humans, animals, and plants even at very low concentrations (1 or 2 µg in some cases). Several individual treatments, namely, physical, chemical, and biological are being implied to remove heavy metals from the environment. But they all face challenges in terms of expensiveness and in-situ treatment failure. Hence, integrated processes are gaining popularity as it is reported to achieve the goal effectively. Integrated processes are the combination of two different methods to achieve a synergistic and an effective effort to remove heavy metals.

(Keywords : Heavy metals, Anthropogenic source, Integrated process, Remediation)

Introduction

Environment comprises of complex variables that includes air, water, and land. Their positive correlation forms a basis for the existence of humans along with other living creatures, namely, plants, animals, and microbes¹. With increase in technological advancement in the form of industrial societies has contributed to severe environmental pollution of air, soil, and water, which are considered to be the indispensable part of human life. Heavy metal pollution is a worldwide problem. Significant concentrations of toxic heavy metals (Cd, As, Fe, Cr, Zn, Cu, Mn, Pb, Ni, etc.) in soil, surface, and

ground water have been reported in various countries like China, Italy^{2,3}. Factors like urbanization, rapid industrialization and increasing population have ended up in generating huge amount of solid waste in various toxic forms which ultimately pollute the entire ecosystem. The disposed wastewaters will also affect the quality of surface water and soil, which on continuous proceeding without proper care may cross permissible limits prescribed by international regulatory agencies^{4,5}.

Heavy metals are regarded as significant environmental pollutants due to high density and high toxicity even at low concentrations^{6,7}. A wide array of toxic heavy metals like As, Cr, Cd, Hg, Pb, etc., disposed by industries will remain as non-degradable and contaminate the soil and water to a greater extent⁸. Because of the high propensity nature of the heavy metals, they tend to accumulate in various environmental matrices, resulting of misleadingly higher concentrations than the prescribed average safety levels^{9,10}. Increased heavy metal concentration can be major sources of many human life-threatening complications such as atherosclerosis, cancer, Alzheimer's disease, and Parkinson's disease, etc.¹¹. This has urged various researchers to develop many technological processes of remediation to bring these contaminant levels within the regulatory limit in the environment (Table 1). Most of the industrial scale remediation involving, physical, chemical, and biological methods are employed as single methods remediation strategies. Such

methods include thermal treatment, adsorption, chlorination, chemical extraction, ion-exchange, membrane separation, electro kinetics, bioleaching etc. Despite the success of these processes, they do face certain disadvantages like low efficiency, high cost and toxic sludge

generation, etc. However, this can be overcome by upgrading them as integrated processes, which has exhibited more efficiency for heavy metal remediation as reported by many researchers in recent years¹²⁻¹⁵.

Table -1
Indian and European standards (EU) standards for heavy metals in soil, food and drinking water^{15, 16}

Heavy Metals	Soil ($\mu\text{g/kg}$)	Food ($\mu\text{g/kg}$)	Water ($\mu\text{g/L}$)	EU Standards soil ($\mu\text{g/g}$)
Cd	3-6	1500	10	3
Cr	-	20000	50	150
Cu	135-270	30000	50	140
Fe	-	-	30	-
Ni	75-150	1500	-	75
Pb	250-500	2500	100	300
Zn	300-600	50000	5000	300
As	-	1100	50	-
Mn	-	-	100	-

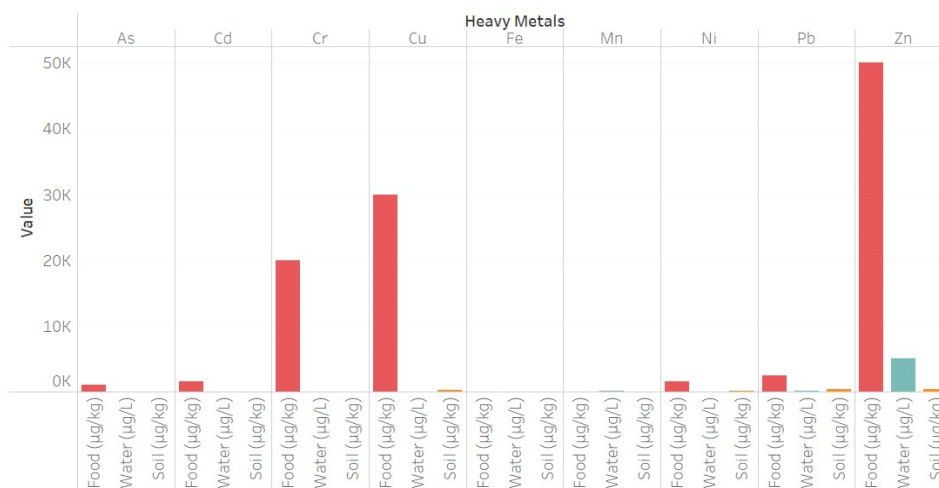


Fig 1: Regulatory limit of heavy metals in Soil, Food and Water

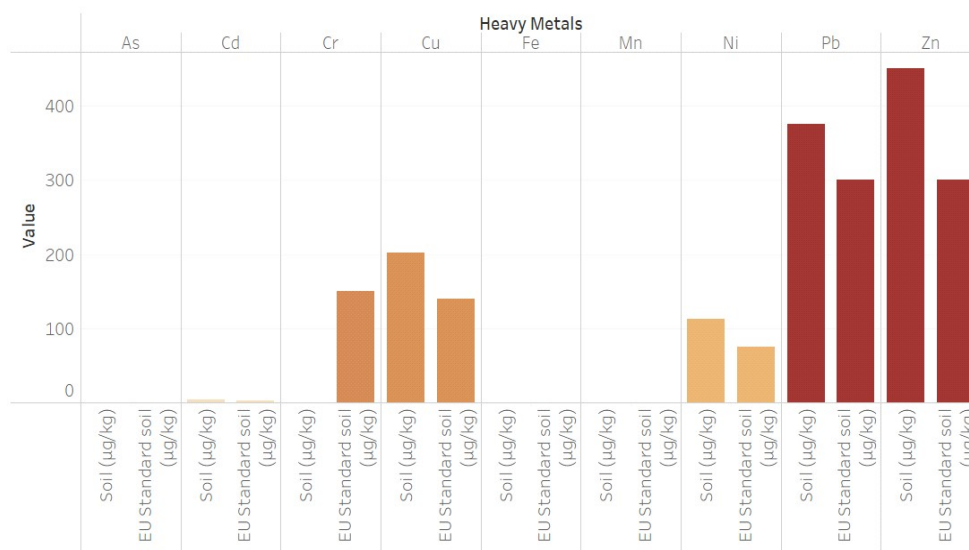


Fig 2: Regulatory Limit of Heavy Metals in soil: Comparison between Indian Standards and EU Standards.

Dispersion of heavy metals in environmental system

The distribution of heavy metals in the environment is a critical area of study due to its profound implications for ecosystem health, human well-being, and sustainable development. Heavy metal pollution is caused as a result of both natural and anthropomorphic activities like mining, smelting, industrial production, using of metals, and metal containing compounds for domestic and agricultural applications. These sources were reported to contribute to human exposure and environmental contamination by various researchers¹⁷⁻²¹.

Soil

Pedosphere is the outermost layer of the soil, where soil formation processes occur, encompassing the topsoil, subsoil, and soil horizons. The soil matrix is a major reservoir or transporting media for heavy metals, because soil and heavy metals associations have rich and diverse binding characteristics. Metals do not biodegrade like organic pollutants, rather they

bioaccumulate in the environment. Soil matrix may adsorb, oxidize, exchange, catalyse, reduce, or precipitate the metal ions²². Soils are contaminated by metals and metalloids from metal wastes, gasoline, animal manure, sludge, waste water irrigation, atmospheric deposition, etc.²³. The most common heavy metals found in soils are Pb, Cr, Zn, Cd, and Hg. Due to bioaccumulation and biomagnification, these metals decrease the crop production and affects the food chain.

Atmosphere

Heavy metals in the atmosphere represent a significant environmental concern due to their potential to adversely impact air quality, human health, and ecosystems. Source of heavy metals in the atmosphere include, mineral dusts, sea salt particles, volcanic eruption, forest fires²⁴, while anthropogenic sources comprise industrial emissions, vehicular exhaust, combustion of fossil fuels, and waste incineration. Air pollutants can thus travel far when entering air circulation and cause global

issues. Soluble particles can then react with the rain and fall into waters and onto land²⁵. Atmospheric heavy metals can contribute to air pollution, especially in urban and industrial areas, posing risks to human health through inhalation and ingestion of airborne particles.

Hydrosphere

The presence of heavy metals in water poses significant environmental and health concerns due to their toxicity, persistence, and potential for bioaccumulation. Heavy metals such as lead, cadmium, mercury, arsenic, and chromium can enter water bodies through various pathways including industrial discharges, urban runoff, agricultural activities, and atmospheric deposition.

Metals present on the surface of soil are carried out from its path, which ends up in sewage and reservoirs²⁶. Rainwater can become contaminated as it passes through the atmosphere. Ground waters are contaminated from landfill leachates, deep well liquid disposal, industrial wastes, etc.²⁷. Factors such as temperature, pH, living organism, cation exchange, evaporation, absorption, etc., will also influence the metal composition in the water¹⁵.

Necessity for heavy metal remediation in the environment

The need for heavy metal remediation in the environment is critical for several reasons. Heavy metals are highly toxic and pose severe threats to the environment and human health¹⁵. Heavy metals like chromium, zinc, arsenic, cadmium, and lead are commonly found in contaminated sites and can accumulate in the food chain, causing damage to biological systems²⁸. Exposure to heavy metals can have serious health effects, including organ damage, developmental issues, and cancer, even at low levels. These metals cannot be degraded and persist in the environment, leading to long-term contamination of soil, water, and sediments²⁹. Regulatory standards for heavy metal concentrations in soil,

water, and food have been established, but these limits are often exceeded, necessitating remediation efforts. Therefore, there is a critical need to remediate heavy metal contamination in the environment using effective, eco-friendly, and cost-efficient methods. Integrated approaches combining physical, chemical, and biological techniques have shown promising results in removing and recovering heavy metals from various environmental matrices³⁰.

Types of integrated processes

1. Physicochemical-Biological Remediation Approach

Physicochemical-biological remediation techniques are a combination of methods that utilize both physical, chemical, and biological processes to remove or degrade hazardous chemicals from the environment.

Physicochemical Methods

Physicochemical methods are used to stabilize or convert pollutants into less toxic forms. These methods include adsorption, membrane filtration, photocatalysis, and advanced oxidation processes. Adsorption utilizes materials possessing extensive surface areas to attach to pollutants, whereas membrane filtration segregates pollutants from water or soil according to their dimensions. Photocatalysis employs light to trigger catalysts, leading to the breakdown of pollutants, while advanced oxidation processes utilize oxidizing agents to disintegrate pollutants.

Biological Methods

Biological methods employ living organisms, such as microorganisms or plants, to degrade or remove hazardous chemicals from the environment. These organisms convert Endocrine-disrupting hazardous chemicals (EDHCs) into less hazardous compounds through metabolic processes. Biological remediation techniques are particularly effective for the degradation of organic pollutants, such

as petroleum hydrocarbons, and can be used in combination with physicochemical methods to enhance their effectiveness.³¹

Combined Approach

A combined approach that incorporates both physicochemical and biological methods can be highly effective in addressing the complex challenges posed by Endocrine-disrupting hazardous chemicals (**EDHCs**) and other pollutants. This approach can involve the use of microorganisms to degrade pollutants, followed by the application of physicochemical methods to remove any remaining pollutants or convert them into less toxic forms.³¹

2. Nanotechnology-Biological Remediation

Nano bioremediation is an emerging and auspicious technique which utilizes nanotechnology to remediate environmental pollutants. Nano bioremediation integrates nanotechnology and bioremediation to create a more effective, faster, and more environmentally-friendly remediation methods^{32,7}.

Nanoparticles (NPs) generated by plants, fungi, and bacteria can be used to remove a variety of organic and inorganic pollutants from contaminated environments.^{32,33,7} The distinctive characteristics of nanoparticles, including their expansive surface area and catalytic prowess, enable them to adsorb, decompose, or alter pollutants with greater effectiveness. Some examples of NPs used in nano bioremediation include zero-valent iron NPs, zinc NPs, noble metal NPs like gold and silver, and copper NPs³⁴. Studies have demonstrated that nanoparticles are effective in breaking down organic pollutants, eliminating heavy metals, and improving phytoremediation processes. Nano bioremediation holds promise for decreasing expenses and time needed to clean extensive polluted areas compared to traditional techniques. Nevertheless, further investigation is necessary to comprehensively grasp the environmental repercussions and destiny of nanoparticles before

broad field implementation. To conclude, the fusion of nanotechnology and bioremediation via nano bioremediation offers a sustainable and environmentally friendly strategy for addressing various environmental contaminants.

3. Electrokinetic Enhanced Phytoremediation

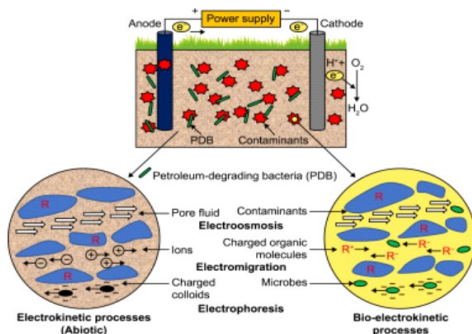
Electrokinetic remediation employs electrical currents to improve the extraction of pollutants from soil that is contaminated. This method involves the application of an electric field to the soil, prompting the pollutants to migrate towards the electrodes for subsequent removal. Electrokinetic remediation is particularly effective for removing heavy metals from low-permeability soils, where traditional remediation methods may not be effective³⁵. Phytoremediation is a natural process that uses plants to remove pollutants from contaminated soil. It is an affordable and environmentally sustainable approach for addressing soil polluted by heavy metals. Phytoremediation involves the use of metal-tolerant plant species that can absorb and accumulate heavy metals in their tissues, reducing their bioavailability and mobility in the soil.³⁶ Electrokinetic enhanced phytoremediation is a technique that combines the benefits of electrokinetic remediation and phytoremediation to effectively remove heavy metals from contaminated soil.³⁷ This integrated method enhances the strength of both the methods for heavy metal removal from soil.

4. Electro-Kinetic Microbial Remediation Approach

In this remediation process, the organic matter is electrochemically converted to generate useful by-products, produce bioelectricity, and fuel by the action of microbial metabolic processes³⁸. As soil contains the majority of heavy metal in insoluble form, their removal rate was minimum, so the solubility can be achieved by coupling electrokinetic with other techniques. On the other hand, if the metal ion was in "soluble" form in the soil, then the remediation rate will be maximized. Based on these

implications, electrokinetic (EK) technique was introduced around 1980s and was widely employed to manage heavy metal contaminated fine grain soils of low hydraulic conductivity³⁹.

In this approach, electrokinetic (EK) technique is combined with biological methods for remediating heavy metal-contaminated soils. It involves applying an electric current to soil to mobilize heavy metals, which can then be removed. This method is cost-effective and has Minimal soil disturbance and ecosystem impacts compared to other methods⁴⁰ but has limitations, such as the bioavailability of metals and mass transfer issues. Integrating EK with biological methods has shown improved efficiency by increasing the bioavailability of pollutants and enhancing biodegradation. Various studies have demonstrated significant removal rates of heavy metals like mercury, zinc, arsenic, copper, and lead using this integrated approach, often employing specific bacteria and sometimes additional nutrients or agents to enhance the process.



(Source: <https://www.sciencedirect.com/science/article/pii/S2666498423000431#BIB22>)

Fig 3- Mechanisms of Electrokinetic Microbial-Remediation in Contaminated Soil.

* The diagram showcases the electro kinetic remediation process using five mechanisms:

electro-osmotic flow, electromigration, electrophoresis, Microbial Degradation, Bio-electrochemical Reactions.

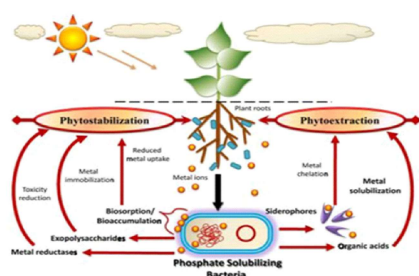
- * The electric field generated by the electrodes mobilizes contaminants and enhances the activity of the degrading bacteria.
- * This dual approach leverages the advantages of both physical and biological mechanisms to achieve efficient soil remediation.

5. Phytobial Remediation Approach

Phytobial remediation is an efficient and eco-friendly solution to remove heavy metals from soil and water. Phytobial based remediation utilizes the plants to uptake the heavy metals and the microbes will help in degradation of those metallic substances⁴¹. Plants uptake the metals, while microbes degrade them through various mechanisms such as bioprecipitation, bioaccumulation, cell surface binding, biotransformation, methylation, solubilisation, biosorption, metal reduction, siderophore secretion, and DNA-mediated interactions. These processes are enhanced by integrating bacteria that secrete plant growth-promoting substances (PGPS) like organic acids, ACC deaminase, siderophores, and biosurfactants. Phytobial remediation has advantages like being a clean, cost-effective approach that can be applied to large contaminated areas like groundwater, soil and sediments⁴². Constructed wetlands are considered one of the most suitable areas for applying phytobial remediation to treat domestic wastewater⁴³.

Limitations of phytobial remediation techniques are:

1. Restricted to shallow aquifer and soil due to plant root length limitations.
2. Potential transfer of heavy metals to the food chain.
3. Long duration, often requiring several seasons.
4. Regular monitoring is needed due to litter fall.
5. Lack of safe and proper disposal methods.
6. Tough metal recovery procedures.



(Source: <https://www.frontiersin.org/journals/environmental-science/articles/10.3389/fenvs.2019.00066/full>)

Fig- 4 Mechanisms of Phytobial Remediation: Interaction between Plants and Phosphate Solubilizing Bacteria in Heavy Metal Removal.

- **Phytostabilization** and **phytoextraction** are the main processes facilitated by plants.
- PSB play a crucial role by producing substances like exopolysaccharides, siderophores, and organic acids to enhance metal immobilization and solubilization.
- The combined action of plants and PSB leads to effective removal and stabilization of heavy metals in the soil.

Future Projects

Future projects in heavy metal remediation are poised to leverage cutting-edge technologies and innovative approaches to address the persistent environmental and health threats posed by heavy metal contamination. Bioremediation techniques could see advancements through genetic engineering of microorganisms and the exploration of plant-microbe partnerships for effective soil and water cleanup. Also, improving cooperation between

stakeholders and the need for better communication and collaboration between scientists, industry, and agricultural stakeholders to improve the performance and implementation of remediation techniques.[44]. Collaboration across disciplines will be paramount for driving forward these efforts and realizing impactful outcomes in heavy metal remediation.

Conclusion

This study explores effective methods for mitigating heavy metal pollution, focusing on innovative approaches such as Physiochemical-Biological Remediation, Nanotechnology-Biological Remediation, and Electrokinetic Enhanced Phytoremediation. Each technique integrates various strategies to tackle heavy metal contamination in different environmental contexts. Physiochemical-Biological Remediation combines physical and chemical processes with biological mechanisms to enhance metal removal. Nanotechnology-Biological Remediation leverages nanomaterials to augment biological remediation efforts for improved efficiency. Additionally, Electrokinetic Enhanced Phytoremediation utilizes electrical currents to enhance plant-based remediation, facilitating the extraction of heavy metals from contaminated soil. These integrated approaches offer promising solutions for addressing heavy metal pollution and restoring environmental quality. In summary, the thorough examination in this review confirms that integrated processes serve as an effective solution. Nonetheless, further research attention directed towards refining the process under real-world conditions is imperative. We anticipate that this review will stimulate increased research interest, potentially leading to innovative remediation endeavours within the research community in the future.

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