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Environmental and human health implications of metal(loid)s: Source identification, contamination, toxicity, and sustainable clean-up technologies

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Environmental pollution is becoming more prevalent in both human life and the ecosystem. The increased use of fossil fuels, mining, and the burning of wastes, as well as industrial wastewater discharge, are polluting natural resources such as water, soil, and air. Metals (loid)s (Cu, Cr, Cd, Zn, Ni, Pb, Hg, Sb, Sn, and As) contribute to several ecological problems when exposed to humans and the environment resulting in serious health and environmental risks. The pollution of aquatic and terrestrial sites with these elements is an issue of environmental as well as public health significance. The present review highlights environmental problems instigated by the toxic metal (loid)s, their source, and respective health/environmental concern along with the importance of creating low-cost, environmentally acceptable clean-up technologies for treating household and industrial wastewater. Various physical, chemical, biological, and/or biochemical as well as their various combinations have been described from the sustainable technological point of view. Techniques such as ion exchange, membrane filtration, photocatalysis, bioremediation, phytoremediation, economical biosorbents, and nanomaterials have been discussed in detail along with respective recent case studies to gain a significant insight towards the solution of the environmental problems focused and action-oriented sustainable

technologies development. Thus, this article significantly provides a deep insight into metal (loid)s toxicity, source identification, and their influences on the ecosystem and human health along with conventional and sustainable clean-up technologies.

KEYWORDS

toxicity, aquatic environment, sustainability, metal(loid)s, clean-up technologies

1 Introduction

The basic necessity across the planet is represented by the environmental significance of water. Water is the most fragile component of our environment, and it is essential for both human and industrial progress. As the population rises, so does the demand for clean water for drinking purposes. This precious resource must be handled in a viable mode to safeguard the expansion of the human population in an environment with limited resources (Boretti and Rosa, 2019). Water resource management is a challenge in many developing nations owing to a lack of integration and a comprehensive strategy, generally with minimal engagement from the general public and other stakeholders other than the government (Loucks and van Beek, 2017).

The severe environmental problem is growing as a result of water pollution and insufficiency, and its restricted availability is growing as a result of the devastation of natural water supplies. During the last 50 years, industrialization has expanded at a rapid pace, increasing the need for indiscriminate exploitation of the Earth's natural resources, and exacerbating the worldwide problem of environmental pollution (Ahmed et al., 2022). Toxins such as organic and inorganic contaminants, organometallic mixtures, radioactive isotopes, and gaseous pollutants have severely polluted the aquatic environment (Briffa et al., 2020). Industrial activities have increased in developing countries in modern times, thus contributing to more metal (loid)s pollution. The metal (loid)s contamination is mostly instigated by the discharge of wastewater from different industries such as power plants, mining, pharmaceutical, metal finishing as well as waste disposal activities (Srivastava et al., 2017; Kinuthia et al., 2020).

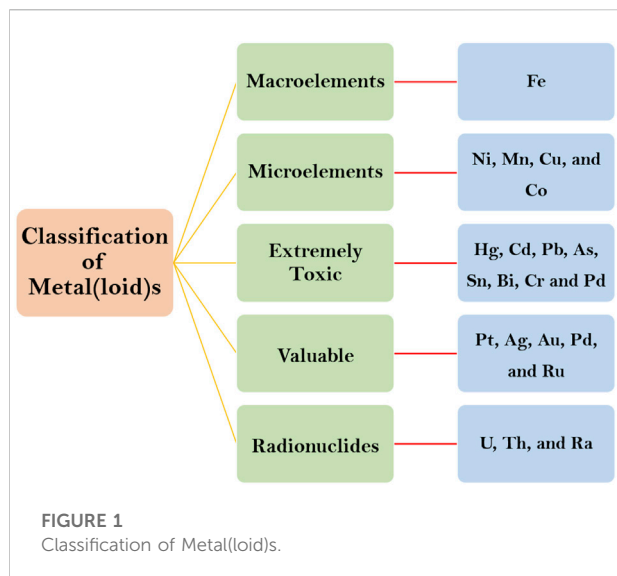
Several water quality issues are waiting to be solved including metal(loid)s, pesticides, fluoride, and many more (Islam et al., 2018a; Wołowicz et al., 2019). Due to the unrestricted release of industrial wastes, raw sewage, and other waste contaminants, the majority of the environment disrupts organism survival and biological activity (Akhtar et al., 2021).

The assurance of clean water is a big challenge. Sustainable technologies are having potential and these technologies can create huge changes. Sustainable technologies are a powerful tool for managing environmental problems and offering remarkable solutions. These technologies are surely a great promise and a

hope for advancements of existing technologies to gain maximum outputs (Rene et al., 2021).

Soil pollution by metal (loid)s is becoming a critical environmental concern due to industrial revolution and urbanization (Alengebawy et al., 2021). The persistent and non-biodegradable nature of metal (loid)s facilitates their accumulation in the soil and can pose harmful effects on the human health (Sarwar et al., 2017). The distribution of metal (loid)s in soils is associated with both natural and anthropogenic inputs. Natural sources include volcanic eruptions, geological weathering of parent rock materials, etc. Whereas, anthropogenic sources of metal (loid)s are extensive use of fertilizers and pesticides in agriculture farms, mining and smelting of metals, industrial emissions, aerosol deposition, spillage of petrochemicals, leaded gasoline and paints, and atmospheric deposition (Chibuikwe and Obiora, 2014). Soils are the primary sink for metal (loid)s released into the environment, where metal (loid)s go through several complex physical and chemical processes such as co-precipitation, adsorption, desorption, metal oxide or hydroxide formation, hydrolysis, and biological uptake (Delshab et al., 2016). Accumulation of metal (loid)s in soil is boosted by the different components such as organic matter, phyllosilicate, carbonate, and charged minerals. Moreover, they show ion exchange with clay particles, where clay minerals bearing several oxides and humic matter form organo-metal compounds, which escalates metal (loid)s accumulation in soil (Violante et al., 2010). All over the world, there are over 5 million areas where metal (loid)s concentrations are now over the allowable levels (Li et al., 2019). Metal (loid)s pollution has induced several threats to the ecosystem and people, and it impacts food chain security (soil-plant-human or soil-plant-animal-human), reduction in food quality *via* phytotoxicity, and diminishing the ability to use the land for agricultural production, all of which have an impact on food security and exacerbate issues of land tenure crises (Gonzalez Henao and Ghneim-Herrera, 2021). Therefore, characterization and clean-up of metal (loid)s contaminated soil are necessary for their effective conservation and restoration. Risk assessment is a potent scientific technique that helps decision-makers to manage highly contaminated areas efficiently and affordably while conserving the ecosystem and human health.

This article scientifically reflects the properties of potentially toxic elements (metalloids) as harmful components in water and soil particularly highlighting their ecological persistence and their toxicity on human health. Further, the article describes several available clean-up technologies such as ion exchange,



membrane filtration, photocatalysis, economical biosorbents, nanomaterials, bioremediation, and phytoremediation for potentially toxic elements (Cu, Cr, Cd, Zn, Ni, Pb, Hg, Sb, Sn, and As).

2 Metal(loid)s

Metal (loid)s is a term used to describe a group of elements having a high molecular weight and density (Punia et al., 2022). These elements are considered major environmental contaminants even in little quantities. Metal (loid)s such as Cd, Ni, Hg, As, Cr, Th, Zn, Sb, Cu, and Pb have a comparatively great density extending from 3.5 to 7 g cm³ (Briffa et al., 2020). Metal (loid)s contamination poses a severe hazard and concern to the bio-network (Hashem et al., 2017). As per USEPA, the eight most prevalent metal (loid)s are lead, chromium, arsenic, zinc, copper, cadmium, nickel, and

mercury (Tchounwou et al., 2012). A broad categorization of metal (loid)s based on their classes is demonstrated in Figure 1.

Metal(loid)s tend to accumulate in the environment which results in their higher concentrations than the allowed limits (Rzymiski et al., 2014). The maximum permissible limit of different metals such as Cr, Cd, Hg, Pb, and Ag in an aqueous medium is 0.01, 0.05, 0.002, 0.015, and 0.05 mg/L respectively, as per the Comprehensive Environmental Response Compensation and Liability Act of the United States (Jaishankar et al., 2014). If the concentrations exceed acceptable levels, they can cause various problems such as Cancer, Alzheimer, and Parkinson disease (Muszyńska and Hanus-Fajerska, 2015). The problem of metal (loid)s contamination has prompted several researchers to create numerous remediation techniques to keep pollution levels below the acceptable limit (Table 1).

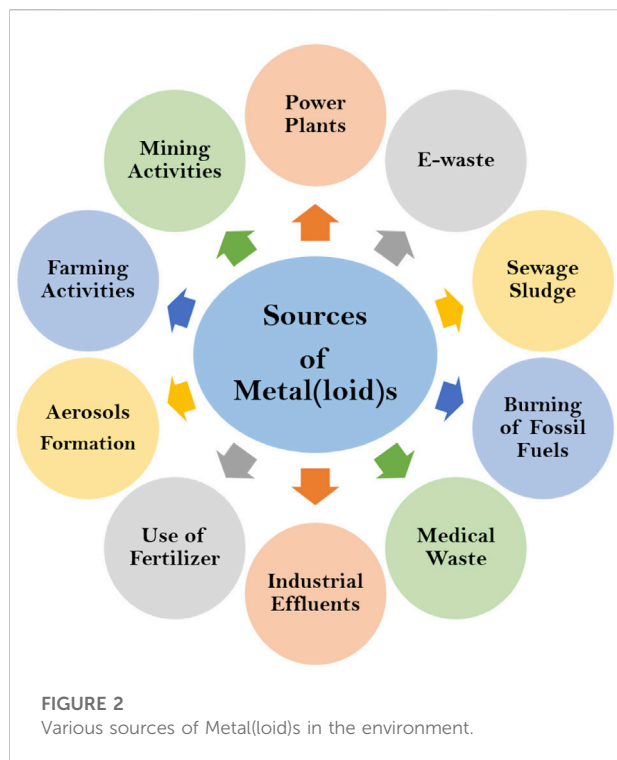
These metal(loid)s are abundant in the earth's shell and are not decomposable. These metals come into the human body *via* air, water, and food. Some of the metal(loid)s have an important role in human metabolism at trace amounts but in higher concentrations, they can cause toxicity (Palansooriya et al., 2020; Ahmed et al., 2022). They can be emitted into the atmosphere via mining and industrial activities and end up adjacent to water bodies and soils (Alengebawy et al., 2021; Elbasiouny et al., 2021).

2.1 Metal(loid)s sources and contamination of environment

Metal(loid)s may originate from both natural/geogenic/lithogenic and man-made sources. Natural causes comprise weathering of metal-containing rocks and volcanic explosions, whereas major man-made sources consist of industrial emissions, excavating, smelting, and agronomic operations such as pesticide and phosphate fertilizer application (Gupta et al., 2019). The burning of fossil oils also leads to metal (loid)s emissions into the environment (Balali-Mood et al., 2021; Chheang et al., 2021).

TABLE 1 Standards criteria for Maximum permissible limits for Metal(loid)s [Source: Kabata-Pendias and Pendias, (2011)^a; Liu et al. (2018)^b; WHO (1996)^c; Denneman and Robberse (1990)^d; Chiroma et al., (2014)^e].

Metal (loid)s	Soil (mg/Kg)	Food (mg/Kg)	Water (mg/L)	Eu standards soil
Cd	0.8 ^{a,c,d}	1.5 ^b	0.01 ^b	≤10
Cr	100 ^d	20 ^b	0.05 ^b	≤200
Co	0.1–50 ^e	30 ^b	0.05 ^b	140
Fe	50 ^e	0.425 ^e	0.03 ^b	-
Ni	35 ^e	1.5 ^b	0.2 ^a	≤100
Pb	85 ^d	2.5 ^b	0.1 ^b	≤200
Zn	50 ^d	50 ^b	5 ^b	≤250
As	1–30 ^{a,c}	1.1 ^b	0.05 ^b	≤50
Mn	290–640 ^a	0.5 ^e	0.1 ^b	-



Metal (loid)s remain in the atmosphere, contaminate food, and create various health concerns (Ali et al., 2019). Paper companies, insecticides, tanneries, metal plating industries, mining activities, and other sectors release metal (loid)s into the environment, which are non-degradable and toxic to biological structures. However, metal (loid)s can be converted into less toxic elements and can persist in either inorganic or diverse forms (Han et al., 2016; Kumar et al., 2017). Landfill leachates, liquid disposal, industrial waste, etc., contaminate the groundwater. Temperature, pH, live organisms, cation exchange, evaporation, absorption, and other factors will all affect the metal (loid)s content of the water (Selvi et al., 2019). Different sources of metal (loid)s in the environment are presented in Figure 2.

2.2 Importance of Metal(loids) in life

Metal(loids) are categorized as essential or non-essential based on their roles in various biochemical and physiological functions. Essential metal(loids) are required for living beings in very little quantities and metal(loids) with no recognized biotic purpose are referred to as non-essential elements (Yan et al., 2020). The essential elements for living beings include Cu, Mn, Zn, and Fe, whereas Cd, Pb, Hg, As, and Cr are toxic and considered non-essential (Crichton, 2017). The chemical elements such as Cu, Fe, Ni, Mn, and Zn are vital for plants for their growth, stress tolerance, production, and functioning of diverse biomolecules like

carbohydrates, chlorophyll, nucleic acids, and secondary metabolites (Rai et al., 2021a). Diseases or abnormal states result from either a shortage or an excess of an important heavy metal. Though, the necessary elements for various kinds of plant species, and microbes may differ. It indicates that an element may be required for one organism but not for another (Yan et al., 2020).

2.3 Environmental and human health risks of Metal(loids)

Metal(loids) are the utmost studied pollutants in the environment. Depending on the quantity and period of exposure, almost every metal(loids) can be harmful to the biotic system. Cr, Ni, Cu, Zn, Pb, Cd, As, and Hg are the utmost harmful metal(loids) in the environment (Egorova and Ananikov, 2017). China proposed Cr, Cd, Pb, As, and Hg as the major contaminants for management in 2009 in their 5-years plan for comprehensive prevention and control of metal(loids) pollution because these metal(loids) can be harmful to humans depending on the amount and exposure time (Fu et al., 2017; Kumar and Fulekar, 2017).

Metal(loids) kills the aquatic organism, and cause oxygen deficiency, and algal blooms (Bashir et al., 2020). Once metal(loids) are dumped into rivers, they become hydrated ions, which are significantly more dangerous than metal ions. Those ions interrupt the enzymatic activities of the aquatic microorganism and make absorption faster. Therefore, metal(loids) removal is required to reduce public hazards (Yan et al., 2020).

Metal(loids) ions such as Cd^{2+} , Pb^{2+} , Hg^{2+} , Ag^+ , and As^{3+} react with bioparticles in the human body to create hazardous chemicals (Shimizu et al., 2019). The toxicity of metal(loids) reduces cerebral and neurological function and harms lungs, and kidneys, loss of memory, and cause allergies in the human body. Cell death is also caused by the production of free radicals, which are responsible for oxidative stress (Wang and Du, 2013; Rai et al., 2019). Table 2 describes potential human health concerns of metal (loid)s.

The toxicity of metal(loids) in the human body, food chains and ecosystems has been considered a serious threat to their safety and integrity. The high-level toxicities of various metal(loids) and their multi-trophic transfer into the ecosystems (agriculture, soil, plants, etc.) are serious issues that need to be addressed (Alengebawy et al., 2021; Sarker et al., 2022). Various global policies are also important to address these issues with the respect to developing and developed countries and the presence of various technologies (Yap and Al-Mutairi, 2022). Various recent reports have been explaining the ecotoxicology of metal(loids), their source, transport, and health-environmental risks (Parker et al., 2022). The human health impact and eco-toxicity of various metal (loid)s are given below.

TABLE 2 Hazardous Impacts of Metal(loid)s on Human Health and their Major Sources.

Metal (loid)s	Effects on human health	Major sources
Pb	Harm to central nervous and blood systems, and also damage to kidney	Paint, pesticides, mining batteries, water pipes, automobile emissions
Cr	Asthmatic bronchitis, DNA damage	Steel, paper, rubber, cement industries, and mining
Hg	Prolonged injury to the brain, respiratory problems	Pesticides, batteries, paper and leather industry, electronics, pharmaceuticals
Bi	Skin problems as well as depression	Alloys, pigments, and pharmaceuticals
Co	Nausea, loss of vision, heart problem, thyroid injury	Coal and Oil burning, cobalt-containing ores, and the use of cobalt-containing chemicals
Fe	High risk of lung tumor	Rock dissolution, acid mine drainage, landfill leachates, sewage
Ag	Brain damage, kidney, eye, lung, and liver associated problems	Photographic industry and disposal of sewage sludge
Ni	Lung cancer, nose cancer, heart disorders	Steel and magnetic industry
Sb	The irritation of the skin and eyes	Mining, smelting waste, tailings dam, and wastewater from the underground tunnel
Cd	Causes neural injury	Welding, electroplating, fertilizers, Cd-Ni batteries

2.3.1 Cadmium

Cadmium (Cd) can be found in the earth's crust together with other elements. Cd is not required for biotic processes. In addition, it is the most hazardous metal found in industrial discharge. It is used extensively in sectors such as electroplating, Cd-Ni batteries, phosphate fertilizers, stabilizers, and composites (Haider et al., 2021). Even at little concentrations, Cd compounds are very toxic and accumulate in the environment. The "Itai-Itai" illness is caused by Cd build-up in the river and causes bone weakening and fractures in humans. It can potentially cause lung cancer as well as damage to the respiratory system, liver, and kidney (Rafati Rahimzadeh et al., 2017; Genchi et al., 2020b).

2.3.2 Chromium

Chromium (Cr) exists as ore, which is made up of ferric chromite (FeCr_2O_4), crocoite (PbCrO_4), and chromeochre (Cr_2O_3). It is widely utilized in the leather industries, as well as in paper, pulp, and rubber manufacture. The high Cr concentrations can affect the liver and kidneys, create skin ulcers and affect the nervous system of humans. Cr (VI) is more hazardous than Cr (III) for human health (Demim et al., 2013; Carolin et al., 2017). Cr (VI) is generally found in the chromate salt manufacturing sector. Cr (III) is beneficial in fat breakdown and shows a vital role in the digestion of sugar (Król et al., 2020; Li et al., 2021).

2.3.3 Lead

Lead (Pb) poisoning is extremely harmful to humans. The higher Pb concentrations have the potential to harm the foetus and be toxic to the central nervous system (Kumar et al., 2020). Pb may be found in the forms of sulphide, cerussite (PbCl_2), and galena. The primary reason for Pb contamination in industrial waste is lead-acid battery discharge. It causes illnesses such as renal and neurological system damage, intellectual disability, and cancer (Qu et al., 2013; Cechinel et al., 2014; Briffa et al., 2020).

Airborne Pb can pollute food by deposition on soils and water (Kumar et al., 2020).

2.3.4 Copper

At high concentrations, Copper (Cu) is often regarded as an extremely toxic metal. It is an essential element for people which has a significant role in enzyme activities, bone formation, and tissue development (Balali-Mood et al., 2021). It is utilized in the fabrication of kitchenware, electric cables, tubes, brass, and bronze. Mining, element manufacture, steel trades, circuits, coating trades, dyes, fertilizers, and other sectors are important contributors to Cu (Gao et al., 2013; Mehta et al., 2015). Cu causes the loss of hair, anemia, renal injury, and headaches and also causes mortality when accumulated in the liver, brain, and pancreas, resulting in mortality (Grzeszczak et al., 2020).

2.3.5 Mercury

Mercury (Hg) is generally found in industrial discharge in several forms, such as elemental mercury (Hg_0), mercurous ion (Hg_2^{2+}), and mercuric ion (Hg^{2+}). In general, a considerable quantity of Hg is supplemented in sectors such as paper and pulp, plastics, chloro-alkali, pharmaceuticals, oil refineries, etc. In its organic form, Hg is a very poisonous metal that has been linked to Minamata illness in Japan (Parham et al., 2012). Hg can harm the kidneys, the brain, the reproductive system, and the respiratory system.

2.3.6 Zinc

Zinc (Zn) contributes to the regulation of biological processes and the functioning of tissues in humans. It protects other metals by acting as a protective coating (Hernández-Camacho et al., 2020). Corrosion can be avoided by adding Zn to the steel. It is used in several manufacturing procedures, including steel production, mining, and coal burning. Although Zn is necessary for humans in trace amounts but it can cause vomiting, skin irritation, fever, and anemia (Cristian et al., 2015).

2.3.7 Nickel

Nickel (Ni) is released from several industrial sources such as printing, electroplating, silver refineries, battery manufacture, and alloy sectors (Demim et al., 2013; Malamis and Katsou, 2013). It is required for human blood cell production; nevertheless, the excessive quantity of Ni is hazardous. Trace quantities of Ni may not harm biological cells, but prolonged exposure to a high quantity may harm cells, reduce weight, and harm the heart and liver. Ni toxicity could result in decreased cell development and cancer (Genchi et al., 2020a).

2.3.8 Arsenic

Arsenic (As) occurs naturally in the earth's crust in the form of arsenite and arsenopyrite across the planet. As is mostly found in groundwater as arsenate and arsenite (Shankar et al., 2014; Awasthi et al., 2017). The movement of As in water is generally controlled by pH and adsorption. As adsorption in aquatic bodies is aided by metal oxides of Fe, Al, and Mn. As has been discovered at significant concentrations naturally in groundwater in India, Bangladesh, Taiwan, Brazil, and Chile. Because of its higher quantity in drinking water, it is hazardous to both people and animals. The groundwater pollution from As initiated by weathering of rocks and sediments, as well as consuming arsenic-contaminated water, causes blood poisoning, lung cancer, and breathing problems (Nicomel et al., 2015; Yeo et al., 2021).

2.3.9 Cobalt

Volcanic outbreaks, ocean spray, and forest fires are all-natural causes of Cobalt (Co) in the environment. Coal-fired power stations as well as car exhaust, are man-made causes of Co in the atmosphere. Co processing operations, the manufacture of cobalt-containing composites, sewages, domestic and agronomic overflow are all important sources of Co to the river ecosystem (Farjana et al., 2019; Dehaine et al., 2021; Horn et al., 2021). The human health consequences of Co are defined by a complicated clinical syndrome that includes neurological, cardiovascular, and endocrine abnormalities (Leyssens et al., 2017).

2.3.10 Iron

Iron (Fe) is a substantial component of the lithosphere, accounting for roughly 5% of the total. It is often discovered in municipal discharge, mainly in locations where Fe and steel are produced. Even at little quantities of around 1.8 mg/L, the taste of Fe in water may be perceived. Iron enters the environment mostly through industrial effluents such as pharmaceutical goods, mining trades, mineral treating, and plating industries (Briffa et al., 2020). The occurrence of Fe(II) in water promotes the proliferation of iron microorganisms, which results in unpleasant water color, taste, and odour. Fe is important for humans for the normal working of the biological system (Güluy et al., 2018). Anemia is caused by Fe deficiency. Excess iron, on the other hand, is harmful to humans. Excessive Fe consumption

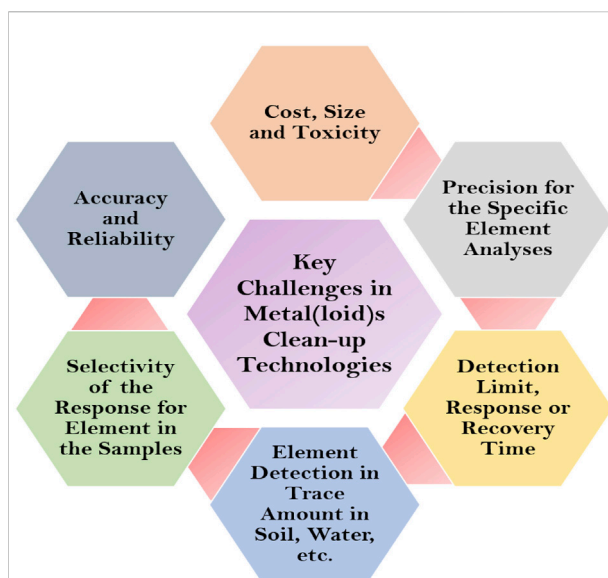


FIGURE 3
Key challenges to improve sustainable technologies for metal(loid)s detection and clean-up from the environment.

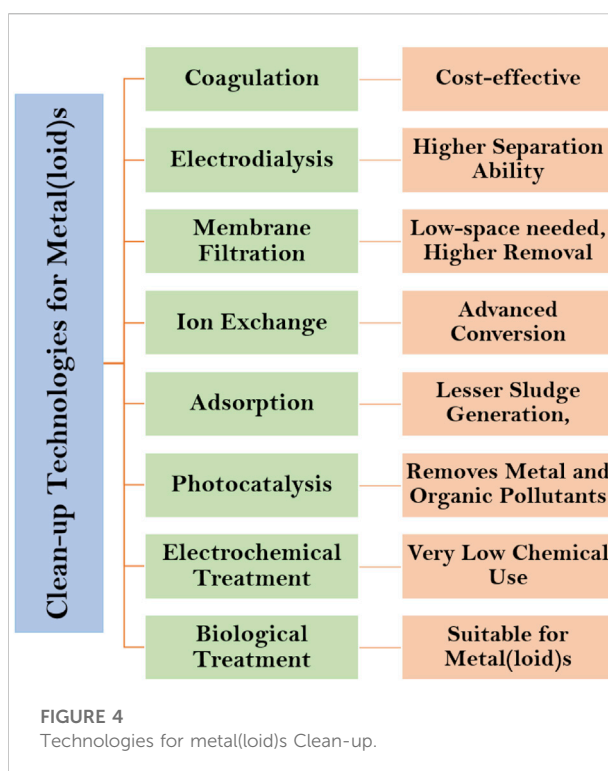


FIGURE 4
Technologies for metal(loid)s Clean-up.

causes haemochromatosis, which causes tissue damage owing to Fe build-up. The first signs of Fe poisoning in humans include vomiting, diarrhea, and intestinal damage (Smith et al., 2017).

TABLE 3 Merits and demerits of clean-up technologies for Metal (loid)s.

Techniques	Advantages	Disadvantages	References
Coagulation	Less expensive, Dewatering potential	Sludge generation and chemicals usages are higher	Ahmed and Ahmaruzzaman, (2016)
Membrane filtration	Higher elimination of metals, low space required	Costly and difficult process	Ahmed and Ahmaruzzaman, (2016)
Adsorption	A smaller amount of sludge generation, use of inexpensive adsorbents	Desorption	Ruihua et al. (2011)
Electrochemical treatment	low chemical usage	Need more electricity	Ahmed and Ahmaruzzaman, (2016)
Electrodialysis	Higher separation of metals	Blockage and energy loss	Nguyen et al. (2013)
Ion exchange	Higher components conversion	long time required	Farooq et al. (2010)
Photocatalysis	Removes inorganic and organic contaminants	long time required	Ihsanullah et al. (2016)
Biological treatment	Useful in heavy metals removal	Necessity to be advanced	Ahmaruzzaman, (2009)
Oxidation	No electricity required	Rusting arises because of oxidation	Patil et al. (2016)

3 Clean-up technologies for metal(loid)s

The metal(loid)s are openly discharged into the environment and affect humans, animals, and plants. The most common routes of contact are breathing and skin interaction in humans. The increasing danger of human exposure to these metal(loid)s has significant health concerns as well as ecological degradation (Rzymiski et al., 2014; Kumar, 2018). Therefore, their detection and clean-up from the environment is a very important aspect (Figure 3). Several clean-up technologies for metal(loid)s removal have been developed during the last few decades (Figure 4).

Since metal(loid)s ion concentrations in the environment repeatedly exceed acceptable limits, therefore many treatment approaches are being applied to protect the environment. Ion exchange, adsorption, filtration, electrodialysis, precipitation, microbiological, electrochemical method, and membrane bioreactors are more interesting and dependable clean-up treatment technologies for these potentially toxic elements (Rajasulochana and Preethy, 2016; Qasem et al., 2021). These techniques are classified as physical technologies, chemical technologies, and biological technologies. Different treatment techniques may vary depending on the types of elements, however, a combination of different techniques may be used for the successful removal of metal(loid)s. Table 3 summarises the merits and drawbacks of these technologies.

3.1 Chemical precipitation

It is the process of adding compounds to convert the physical state of dissolved particles to enable their removal *via* sedimentation (Pohl, 2020). These precipitates are separated during the sedimentation process, and the residual solution is utilized for various uses. It is a proficient way of removing Cu, Cd,

Mn, and Zn. Tanong et al. (2017) examined the removal of Ni and Mn by the addition of Na_2CO_3 , which was shown to be fully precipitated at pH 9. To eliminate precipitates from water, further techniques such as filtering and sedimentation are necessary. The treated water may then be used again or released into the environment. Though, this procedure needs a huge number of compounds to precipitate the metals. They are commonly applied in industries due to their simplicity and cost-effectiveness. Hydroxide and sulphide precipitation are the modern chemical precipitation processes (Estay et al., 2021). Several researchers have used different techniques involved in chemical precipitation for removing metal(loid)s from wastewater with the application of different materials (Table 4).

3.1.1 Hydroxide precipitation

Chemical precipitation of metal(loid)s as hydroxides using lime or sodium hydroxide is extensively applied due to its ease of handling and low cost. The metal hydroxides that are inexplicable in the alkaline medium are increased when the pH is changed. For metal(loid)s removal, layered double hydroxides are produced in the case of trivalent ions (Thomas et al., 2021). To create a hydroxide precipitate, several precipitants such as lime, calcium hydroxide, ammonium hydroxide, and sodium hydroxide are presented. Due to their ease of accessibility, lime and limestone are often employed (Kumar and Jana, 2021). The drawbacks of this approach include differences in the optimal pH for hydroxide production across metals, which may cause issues in the treatment of effluents comprising mixed metal ions. Other disadvantages include variable metal hydroxide solubility at a given pH and the production of a considerable sludge volume (Vidu et al., 2020).

3.1.2 Sulphide precipitation

Sulphide precipitation can provide better metal (loid)s removal because most metal(loid)s create stable sulphides. The

TABLE 4 Application of different materials used in the chemical precipitation technique for metal(loid)s removal.

Technique used	Targeted Metal (loid)s	Material applied	References
Hydroxide Precipitation	Fluoride metals	Ca(OH) ₂ , Mg(OH) ₂ , and CaCl ₂	Jadhav et al. (2014)
	Fe	NH ₄ OH	Maila et al. (2014)
	Zn ²⁺	Lime	Ghosh et al. (2011)
	Mn	NaOH	Zhang et al. (2010)
Sulphide Precipitation	Mn, Al, Mg, Zn, Sr, Co, Ni, Sb, Sn, Fe, Cu, Pb, Hg, Ce, and Cd	Solid Na ₂ S and Na ₂ S solutions	Prokkola et al. (2020)
	Ni	Sulphide and sulphate reducing bacteria (<i>Desulfovibrio vulgaris</i>)	Mansor et al. (2019)
	Cu and Zn	Biological and synthetic sulphide	Mokone et al. (2012)
Carbonate Precipitation	As, Ba, Cr, Cu, and Zn	CaCO ₃	Hunter et al. (2021)
	Ni and Cu	Na ₂ CO ₃	Junuzovic et al. (2019)

benefit of employing sulphide precipitation is that sulphide precipitate is less soluble in alkaline conditions than hydroxide precipitate. Solid (ferrous and calcium sulphide), aqueous (sodium sulphide, sodium hydrosulphide, ammonium hydrosulphide), or gaseous sulphide sources (hydrogen sulphide) are the most commonly utilized sulphide precipitants (Günes et al., 2021).

3.1.3 Carbonate precipitation

Metal carbonate precipitation using Ca or Na carbonates is relatively limited. Several scientists described superior results for Cd (II) and Pb (II) from electroplating wastes using carbonate precipitate. Once the pH was raised to 7.5, the remaining Pb (II) and Cd (II) concentrations were 0.60 and 0.25 mg/L, correspondingly (Egbosiuba et al., 2021).

3.2 Membrane filtration

It is a pressure-driven technology that is now applied in the treatment of wastewater. This process includes disinfection in addition to metal(loid)s removal (Lyu et al., 2016). The purification process may be accelerated by treating the membrane with chemical substances. The membrane is constructed of a permeable substance that shows a vital part in metal(loid)s removal from wastewater (Patil et al., 2016). Membrane materials are divided into ceramic and polymer. Ceramics, due to their chemical resilience are mostly employed for industrial wastewater treatment. It is a favourable technology for metal(loid)s removal due to its effectiveness and easy process as compared to other methods. It is also effective in removing suspended particles and chemical substances. Despite its benefits, membrane filtration is restricted to metal(loid)s elimination due to membrane fouling, frequent membrane replacement, and high cost (Kotobuki et al., 2021). Membranes are complicated structures that incorporate nanometer-scale active components. The partitioning of water and dissolved salts across

the membrane are impacted by the chemical characteristics and the physical structures of the membrane on nano to microscales. This transitional range comprises colloidal solids, big organic molecules, and polymers from the standpoint of filtration. Ultrafiltration, nanofiltration, electrodialysis, and reverse osmosis are the membrane techniques applied to clean up the metal (loid)s (Khulbe and Matsuura, 2018; Algieri et al., 2021). Different types of membranes applied by the researchers for metal(loid)s clean-up have been illustrated in Table 5.

3.2.1 Ultrafiltration

Ultrafiltration is a separation technology that uses less energy to clean wastewater. This technique removes particles in the 10–100 nm size range. The particles quickly separate from the aqueous solutions due to hydrophobic and electrostatic interfaces. Since it has a bigger hole size membrane that is larger than metal(loid)s ions size, this technology is usually utilized in the form of a combination technique. Thus, the metal(loid)s ions can readily flow through the UF membrane. Chemical and polymeric agents were employed to increase the ultrafiltration process, which is known as micellar-enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF) (Warsinger et al., 2016; Naseem and Durrani, 2021). MEUF was developed in the 1980s and used to remove the metal(loid)s and organic pollutants from the wastewater. It is a good separation method for extracting metal(loid)s. Surfactants adding is the simple principle of this method (El Batouti et al., 2021). Samper et al. (2009) utilized micellar-enhanced ultrafiltration to eradicate Cd²⁺, Pb²⁺, Ni²⁺, Zn²⁺, and Cu²⁺ from synthetic water in a lab-scale system utilizing SDS and linear alkylbenzene sulfonate (LAS). PEUF is presented as a sustainable technique for extracting metal(loid)s ions from an aqueous medium. It employs a water-soluble polymer with a greater molecular weight than complex metallic ions and produces macromolecular (Meng et al., 2021; Oyarce et al., 2022). Lin et al. (2020) applied micellar-enhanced ultrafiltration (MEUF) to extract Ni ions from aqueous

TABLE 5 Different membranes applied in the membrane filtration technique for the removal of metal (loid)s.

Technique used	Targeted Metal (loid)s	Membrane applied	References
Ultrafiltration	Hg (II)	Polyvinylamine-amplified ultrafiltration	Huang et al. (2015)
	Ni and aniline	Micellar-enhanced ultrafiltration (MEUF) polysulfone, NP010, and UFX5	Tanhaei et al. (2014)
Reverse osmosis	Ni, Cu, Pb, Cd, and Cr	Membrane bioreactor coupled through the reverse osmosis method	Dialynas and Diamadopoulos, (2009)
	Cu (II) and Ni (II)	Reverse osmosis + (Na ₂ EDTA) as a chelating agent	Mohsen-Nia et al. (2007)
Nanofiltration	Zn, Cu, Fe, and Pb	–	Marecka-Migacz et al. (2020)
	Zn, Cd, Pb, Cu, and Fe	Ceramic membrane	Nedzarek et al. (2015)
	Pb	Polyamide nanofiltration membrane	Mehdipour et al. (2015)
	Pb, Cu, Ni, Cd, Zn, and As	Tinny film composite membrane proliferated by the poly (amidoamine) dendrimer (PAMAM)	Zhu et al. (2015)
	As	Nanofiltration membranes (NF90 and N30F)	Figoli et al. (2010)

solutions, utilizing the surfactant sodium dodecyl sulphate (SDS) as a chelating agent. Using the Box-Behnken design, a response surface method was applied to model and optimize process variables and indicators. The response surface method might sufficiently represent the performance pointers within the evaluated ranges of the procedure variables, according to experimental verification. To estimate MEUF performance and confirm the RSM results, an artificial neural network (ANN) model was used. The generated ANN models suited the experimental data well.

3.2.2 Reverse osmosis

This method employs a semi-permeable film which permits the cleansed liquid to flow while rejecting impurities. It helps in removing the different microorganisms from water and is also responsible for about 20% of the world's salt removal capability. The pore size of a RO membrane ranges from 0.1 to 1.0 nm. It's commonly utilized in the desalination process (Feria-Díaz et al., 2021). The capacity of a RO membrane is determined by the membrane's composition, temperature, pressure, pH, and clogging properties. To prevent membrane entangling, the wastewater is pre-treated, which eliminates shallow and colloidal particles. This technology has been exclusively applied in water treatment for the past 10 years (Obotey Ezugbe and Rathilal, 2020). Petrinic et al. (2015) reported that the wastewater treatment from the metal finishing sector utilizes integrated membrane techniques like ultrafiltration and reverse osmosis to eliminate suspended particles and metal(loid)s. This dual membrane technique eliminates 91.3 percent to 99.8% of pollutants from effluent, including metals, organic and inorganic composites, and the ultrafiltration reduces fouling of the RO membrane.

3.2.3 Nanofiltration

Nanofiltration is a pressure-driven technique and is widely utilized in the chemical and biotech sectors. It is a technology that

falls in between reverse osmosis and ultrafiltration. The benefits of this technique include low energy consumption, efficiency, and easiness of operation. It also requires less pressure than reverse osmosis (Tao et al., 2016; Abdel-Fatah, 2018). Its effectiveness is determined by pH, temperature, membrane propensity, and design (Hosseini et al., 2016). The membranes are typically prepared by synthetic polymers and externally charged, which aids in the dissociation of metal (loid)s. Size exclusion and charge exclusion are the separation mechanisms used in nanofiltration (Siddique et al., 2020; Suhaimi et al., 2022). This technology is favourable for eliminating metal (loid)s from wastewater, including Ni (Murthy and Chaudhari, 2008), Cr (Muthukrishnan and Guha, 2008), Cu (Ahmad and Ooi, 2010); and As (Nguyen et al., 2009; Figoli et al., 2010).

3.3 Chemical coagulation/flocculation

Coagulation/flocculation might be used to clean up the metal(loid)s from wastewater, (Tang et al., 2016). The coagulation treatment disrupts colloidal elements by applying a coagulant, resulting in sedimentation. In general, coagulation is trailed by flocculation of the unsteady elements into large flocs to enlarge particle size (Teh et al., 2016). The enormous flocs will finally settle in the sedimentation tank. Alum, ferric chloride and ferrous sulfate are widely utilized in conventional wastewater treatment systems (Shewa and Dagnew, 2020). This technique has a few drawbacks, such as high functioning expenses owing to the broad utilization of chemicals. Macromolecule flocculants are being applied as efficient flocculants for metal(loid)s remediation from wastewater (Maćczak et al., 2020; Jiang et al., 2021). Shen et al. (2015) investigated the removal of Cr (III), Zn (II), and Cd (II) metal ions using flocculation. Cationic polymers and anionic surfactants were applied in the investigation. The resulting structure uses cationic polymers and anionic

surfactants known as polymer-surfactant aggregates (PSAs). These PSAs exhibited the capability to eliminate metal(loid)s from the system. Diallyldimethylammonium chloride (PolyDADMAC) or poly ethylenimine (PEI) and sodium dodecyl sulphate (SDS) were used as cationic polymers and anionic surfactants respectively. All three elements were easily removed using this system and 99% of efficiency was achieved in 20 min under optimum conditions. Pang et al. (2011) used aluminium sulfate, polyaluminium chloride, and magnesium chloride coagulants for the removal of Pb, Zn, and Fe. Koaret PA 3230 was also used as polyelectrolyte in the experiment. The individual metal and the mixture of selected metals along with pH effect, the dosage of coagulant, and flocs settling time were examined. The outcomes concluded that PACI was found to be the most effective coagulant among all three coagulants.

3.4 Ion-exchange

It is a separation technique that replaces one ion with another for treating wastewater with higher metal(loid)s ion elimination efficiency with less sludge production as compared to the coagulation process (Luhar et al., 2021). Ion exchange resin is a metal(loid)s recovery or removal substance divided into two groups: synthetic resins and natural resins. Both resins are used to swap metal ions with cations. Synthetic resins are far more preferred for infinite metal separation. The main usage of synthetic resins is to remove As from wastewater. Fouling of the matrix happens in the presence of an extremely rigorous metal solution, which is a drawback of these resins (Dixit et al., 2021). Zeolites and silicate minerals are extensively utilized to eradicate metal(loid)s from wastewater in addition to manufactured resins because of little price and availability. Several studies have shown that zeolites have high cation-exchange abilities for metal(loid)s ions in various conditions (Jiang et al., 2018; Morante-Carballo et al., 2021). The foremost constraints of ion exchange are the higher cost and the need for adequate pre-treatment schemes. It can deliver metal(loid)s ion concentrations down to parts per million (Crini and Lichtfouse, 2019). Thakare and Jana (2015) applied high-density ion exchange resin (INDION225H) in aqueous media to remove Cu (II). The physical properties of adsorbent, equilibrium, kinetic and thermodynamic investigations have been carried out. The surface of INDION225H resin is made up of 49.9% carbon, 36.1% oxygen, 13.8% sulphur, and 0.18% copper. The equilibrium results indicated 79.49 kJ/mol activation energy for Cu (II) ion adsorption and Freundlich as well as Redlich–Peterson Isotherm followed by the system. Pseudo first and second-order kinetic was responsible for adsorption phenomena. The rate of reaction rises with the primary concentration of metal. The adsorption of metal also depended on the temperature of the system. Zewail and Yousef (2015) eliminated Ni (II) and Pb (II) metal ions using

cation exchange resins (AMBERJET 1200 Na). The batch conical air spouted bed was used for the investigation purpose. The findings indicated that 98 and 99% of Ni (II) and Pb (II) metal ions were easily removed under optimum conditions. The air velocity, time, and primary concentration of metals were also examined during the experiment. The findings recommended that the pseudo-second-order kinetic model easily explains the adsorption phenomena under investigation.

3.5 Electrodialysis

Electrodialysis (ED) is a membrane technology that uses an electric field as a dynamic force to discrete ions through charged films (Gurreri et al., 2020; Shen and Badireddy, 2021). Ion-exchange membranes are engaged in the majority of ED procedures. Cation and anion-exchange membranes are two categories of membranes. This method is being extensively utilized to produce drinking water from seawater, as well as to treat industrial effluents, recover valuable minerals, and produce salt. This process has similarly demonstrated a potential technique in the treatment of metal (loid)s (Hassanvand et al., 2017). Sivakumar et al. (2014) remediated Cd and Sn using electrodialysis. The trial was performed at a different temperature and agitation speed and this method easily removed the metal(loid)s ions present in the electroplating wastewater. Both the metal(loid)s ions easily disappeared within 8 h of reaction at 50°C and 100 rpm. This study established that the electro-dialysis technique magnificently reduced Cd and Sn from wastewater collected from the electroplating industry. Moura et al. (2012) removed Cr using the electrodialysis method. The effluent samples were collected from the metal finishing and tannery industry. The two different prepared membranes (MCS and MTS) and one commercial membrane (Nafion 450) were used for comparative analysis. The findings concluded that all three membranes were having almost similar efficiency for tannery effluents whereas Nafion 450 showed superior efficiency than MCS and MTS in the case of metal finishing samples.

3.6 Electrochemical treatment

Electrochemical techniques can recuperate metal(loid)s in their elemental state by plating out ions on a cathode surface. Because electrochemical wastewater systems need a relatively substantial financial investment as well as a costly energy source, they have not been extensively used. However, because of severe environmental laws governing wastewater disposal, electrochemical methods have regained prominence globally (Rai et al., 2021b; Zavahir et al., 2021). Zuo et al. (2020) used MOF@rGO nanocomposite electrode material to remove Pb (II). In a typical electrochemical treatment method, rGO and

TABLE 6 The application of different adsorbents for the removal of metal (loid)s.

Clean-up technique	Metal (loid)s	Adsorbents applied	References
Activated carbon adsorbents	Pb	AC filter oxidized by (NH ₄) ₂ S ₂ O ₈ solutions	Mena Aguilar et al. (2016)
	Pb ²⁺ and Cd ²⁺	Activated carbons from grape industrial wastes	Sardella et al. (2015)
	Pb ²⁺ , Cu ²⁺ , Cr ³⁺ , and Cd ²⁺ .	Moso and Ma bamboo-activated carbons	Lo et al. (2012)
	Cu ²⁺ and Pb ²⁺	Eucalyptus bark-derived activated carbon	Kongsuwan et al. (2009)
Carbon nanotubes adsorbents	Cr (VI) and Cd (II)	Carbon nanotubes and activated alumina nanofloral clusters (NCs)	Sankararamakrishnan et al. (2014)
	Cu (II), Pb (II), Cd (II), and Zn (II)	MWCNT modified with 8-hydroxyquinoline	Kosa et al. (2012)
Algal biomass	Cu ²⁺ , Cd ²⁺ , Cr ³⁺ , and Pb ²⁺	Marine algae <i>Ulva lactuca</i> powder and <i>Ulva lactuca</i> activated carbon	Ibrahim et al. (2016)
	Cd (II) and Pb (II)	Anabaena sphaerica	Abdel -Aty et al. (2013)
	Pb (II) and U (VI)	Cystoseira indica	Moghaddam et al. (2013)
Fungal biomass	Cu (II), Cr (II), Cd (II), Pb (II), and Zn (II)	Trichoderma brevicompactum QYCD-6	Zhang et al. (2020)
	Zn (II), Co (II), and Cd (II)	NaOH-treated dry biomass of <i>Aspergillus niger</i>	Hajahmadi et al. (2015)
	Pb, Cd, Ni, and Zn	Mucor rouxii	Yan and Viraraghavan, (2008)
	Cu(II), Cd(II), Zn(II), Cr(III), Mn(II), Pb(II), and Ni(II)	Proteobacteria	Fathollahi et al. (2021)
Bacterial adsorbent	U(VI)	Bacillus amyloliquefaciens	Liu et al. (2019)
	Cr (VI)	Escherichia coli with waste tea biomass	Gupta and Balomajumder, (2015)
Agricultural residues or plant material	Pb, Cu, Cd, Ni, and Zn	Myriophyllum spicatum compost	Milojković et al. (2016)
	Zn(II), Cd(II) Ni(II), Cr(III), and Fe(II)	Dicerocaryum eriocarpum	Jones et al. (2016)
	Cu, Ni, Cr, and Zn	Moringa aptera gaertn	Matouq et al. (2015)
	Pb (II)	Phytolacca americana L.	Wang et al. (2018)
	Pb, Cu, Zn, and Ni	Musa sapientum	Ashraf et al. (2011)

Co-MOF endow the conductivity and selectivity for the process. MOF@rGO functioned as the cathode in the cell. The results revealed the reduction of Pb (II) concentration from 50 to 0.21 ppm. Song et al. (2019) applied the chronoamperometry method for the removal of As (III). The double potential step chronoamperometry approach was used for adsorption and oxidation of As (III). Initially As (III) has been easily converted into H₂AsO₃ (deprotonated from). At basic pH (pH = 10), this deprotonated easily adsorbed and oxidized into As (V). In a very simple electrochemical removal of As, 91% efficiency was achieved under experimental conditions.

3.7 Adsorption

Adsorption is currently regarded as a viable and low-cost approach for treating wastewater. This technique is flexible in terms of functioning, and it produces high-grade treated waste in many situations. Furthermore, since adsorption is occasionally rescindable, adsorbents could be renewed using an appropriate desorption method (Younas et al., 2021). Several researchers have conducted different metal (loid)s removal studies and they have used various types of adsorbents such as activated carbon, carbon

nanotubes, and biosorbents like algal biomass, fungal biomass, bacterial adsorbent, and agricultural residues (Table 6).

3.7.1 Activated carbon adsorbents

Adsorbents based on activated carbon are commonly utilized to remove metal(loid)s. Its utility stems mostly from its enormous micropore and mesopore contents, as well as the consequent high surface area. Many researchers are investigating the application of alternate current for the removal of metal(loid)s (De Gisi et al., 2016; Lucaci et al., 2019; Petrovic et al., 2021).

3.7.2 Carbon nanotubes adsorbents

CNTs (carbon nanotubes) were discovered by Iijima in 1991 and received great attention due to their exceptional characteristics and uses. Because of their excellent characteristics and applications, CNTs adsorbents are extensively employed in the removal of metal(loid)s (Carolin et al., 2017). CNTs have shown a higher ability for eradicating Pb Cd, Cr, Cu, and Ni (Badawi et al., 2021). There are two kinds of carbon nanotubes (CNTs): 1) single-walled CNTs (SWCNTs) and 2) multi-walled CNTs (MWCNTs) (Odom et al., 1998). These methods are complex due to electrostatic force, precipitation, and chemical interface amid metal(loid)s ions

TABLE 7 Phytoremediation Technologies along with specific plants and targeted metal(loid)s.

Technology	Targeted Metal (loid)s	Plant species	References
Phytoextraction	Cd and Zn	<i>Pennisetum purpureum</i>	Yang et al. (2020)
Phytoextraction	Cu	<i>Boehmeria nivea</i>	Rehman et al. (2019)
Phytoextraction	Cd	<i>Atriplex nummularia</i>	Nedjimi, (2018)
Phytoextraction	Cd	<i>Atriplex lentiformis</i>	Eissa, (2017)
Phytoextraction	Zn and Pb	<i>Armeria arenaria</i>	Frérot et al. (2006)
Phytostabilization	Zn and Pb	<i>Pistacia lentiscus</i>	Concas et al. (2015)
Phytostabilization	Pb	<i>Brassica juncea</i>	Meyers et al. (2008)
Phytodegradation	PAHs	<i>Rhizophora mangle</i>	Sampaio et al. (2019)
Rhizofiltration	Cr and Zn	<i>Salvinia molesta</i>	Kodituwakku and Yatawara, (2020)
Rhizofiltration	As	<i>Salvinia molesta</i>	da Silva et al. (2018)
Phytovolatilization	As	<i>Arundo donax</i>	Guarino et al. (2020)
Phytovolatilization	Hg	<i>Brassica juncea</i>	Moreno et al. (2005)
Phytovolatilization	Se	<i>Stanleya pinnata</i>	Parker et al. (2003)

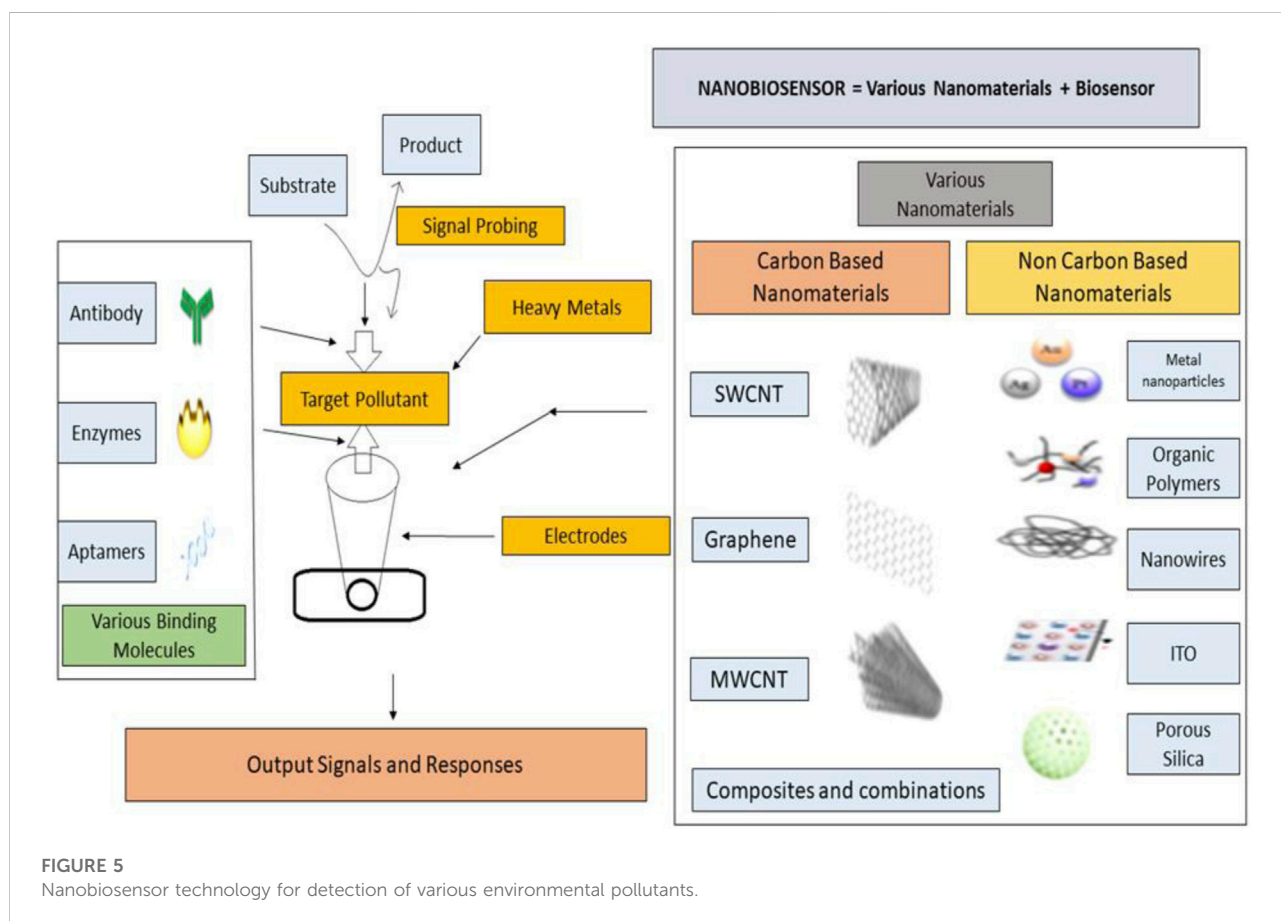


FIGURE 5 Nanobiosensor technology for detection of various environmental pollutants.

and CNT external functional sets. The presence of carbon nanotubes might influence the metabolic action of microorganisms, posing a health hazard to humans (Tran and Mulchandani, 2016; Arora and Attri, 2020; Rahamathulla et al.,

2021). With regards to sensitive detection a novel technology, the Nanobiosensor, and associated advancements are very effective and in trend to detect trace amounts of pollutants (Figure 5). The combination of biology with nanotechnology has allowed the

sensing technology to enable faster, cheaper as well as more reliable evaluations and applications in various scientific domains specifically metal (loid)s detection.

3.7.3 Biosorbents

Biosorption is a novel technology for eliminating metal(loid)s from wastewater. This technique is thought to be an operational and detoxifying procedure even at low concentrations of metal(loid)s. Biosorption is a type of adsorption procedure that involves both solid and liquid states. To remove metal(loid)s, both viable and nonviable biological organisms are required (Saravanan et al., 2022). The main benefit of employing dead material over viable material is that it does not need any growing medium. Because of their high effectiveness and cheap cost, possible sorbents such as bacteria, yeast, fungus, algae, sawdust, seed shells, sugar beet pectin gels, and potato peels are utilized in this process (Bădescu et al., 2018; Okoro et al., 2022; Savastru et al., 2022).

3.7.3.1 Algal biomass

The investigators have focused on both living and non-living algal biomasses for metal(loid)s remediation (Diep et al., 2018). The adsorption capability of living biomass is restricted in metal(loid)s elimination due to the adsorption procedure occurs during the growth phase and metal(loid)s absorption occurs during this phase alone, which is regarded as an intracellular procedure with more sophisticated adsorption mechanisms (Gupta and Diwan, 2017; Igiri et al., 2018; Medfu Tarekegn et al., 2020). However, for non-living algal biomass, the extracellular procedure occurs because the metal(loid)s become adsorbent on the cell wall. The adsorption ability of non-living algae could be influenced by pH, temperature, and interaction duration, among others (Mohammed et al., 2019).

3.7.3.2 Fungal biomass

Due to the higher fraction of cell wall components in fungal biomass, it has a high sorbing ability. It can grow in its native habitat (Garcia-Rubio et al., 2020). The cell wall is composed of chitin, glucan, mannan, proteins, and other polymers, which increase the fungi's adsorption prospective (Blaga et al., 2021). Metal (loid)s can be absorbed by fungi *via* intracellular precipitation, valence conversion, ion exchange, and complexation (Ayangbenro and Babalola, 2017).

3.7.3.3 Bacterial adsorbent

The wastewater treatment via bacterial adsorbent is an excellent biological method. Bacteria have features such as lower size, accessibility, and tractability, which prompts investigators to emphasize microbial adsorbents for metal (loid)s removal (Younas et al., 2021). Bacterial cell walls include functional groups such as ketones, aldehydes, and carboxyl groups and its biomass is typically utilized as a

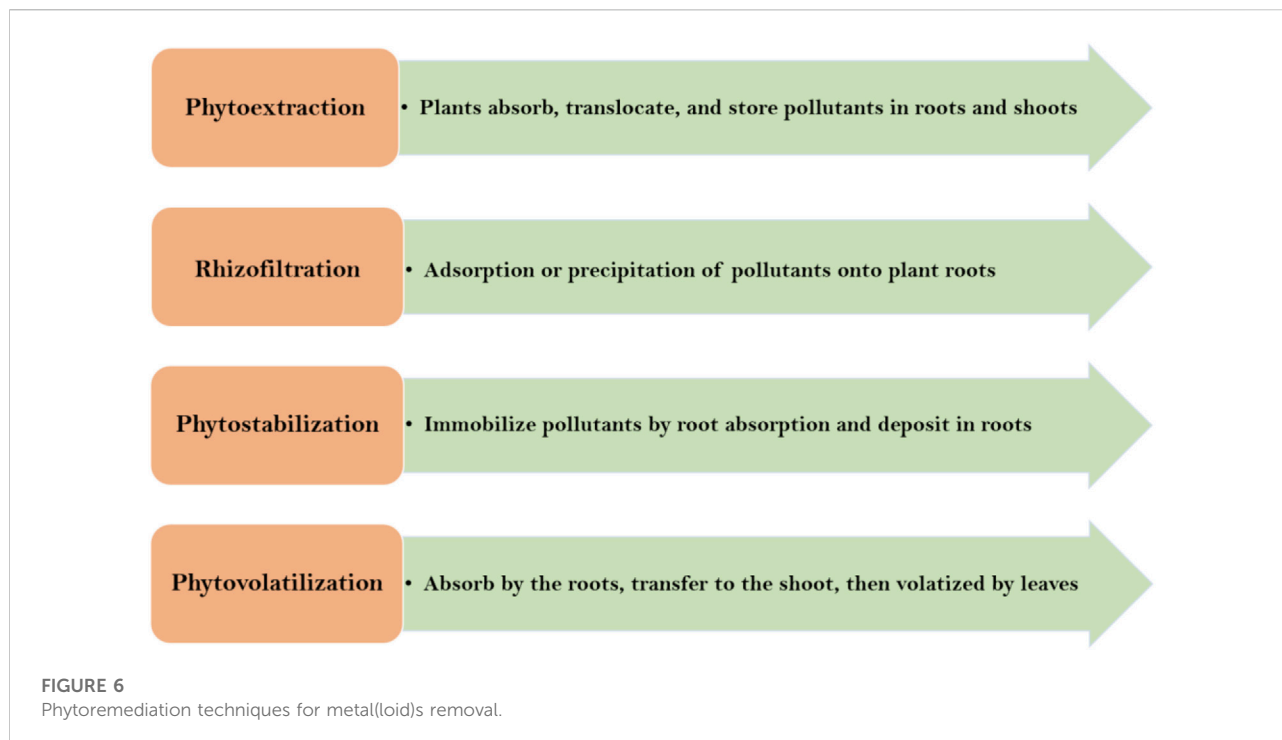
binding or supportive material to the adsorbent for metal(loid)s removal (El-Naggar et al., 2018).

3.7.3.4 Agricultural residues or plant material

Although the adsorbents mentioned above are cheap and renewable, they may have a disposal difficulty and the least commercial benefit. As a result, the researchers focused primarily on the usage of cost-effective adsorbents such as agricultural residues, industrial by-products, and natural compounds for metal(loid)s remediation. It develops an alternative to activated carbon by employing these low-cost adsorbents. The application of low-cost adsorbents is being inspected as a low neutralization method for treating wastewater (Saleem et al., 2019; Sabzehmeidani et al., 2021). The use of agricultural residues in the biosorption technique is an eco-friendly procedure. These agricultural residues or plant materials act as a replacement for traditional adsorbents (Torres, 2020). It is a suitable choice for metal(loid)s removal because the waste becomes more efficient after using these agricultural residues. Agricultural waste such as cashew nut shells, palm oil fruit shells, orange peel, kenaf fiber, and barley straw may be applied for the recovery of metal(loid)s from wastewater (Kwikima et al., 2021).

3.8 Sustainable green technologies for Metal(loid)s clean-up

The sustainable biotic approach to remove metal(loid)s includes: 1) using microbes to detoxify metal(loid)s through valence conversion, extracellular chemical precipitation, or volatilization, and 2) using specific plants to purify the water or soil by deactivating metal (loid)s in the rhizospheric zone or transfer them to the above-ground parts of plants. Phytoremediation is an attractive choice with the respect to the cost as many times the use of selective absorbents or tailoring agents or modification agents etc. made other techniques comparatively cost-enhancing (Sharma et al., 2016). It may remove metal(loid)s, radionuclides, and organic contaminants. Phytoremediation is an inexpensive, proficient, environmentally friendly, and *in-situ* technology (Nedjimi, 2021). The capability to accumulate metal(loid)s varies substantially between plant species because each plant species has a specific mechanism to remove metal(loid)s ions based on genetic, morphological, physiological, and anatomical features (Kumar Yadav et al., 2018; Suman et al., 2018). Depending on the remediation technique, several phytoremediation approaches such as phytoextraction, rhizofiltration, phytostabilization, and phytovolatilization are illustrated in Figure 6 and their strategy is presented in Figure 7. Some specific plants species used in the phytoremediation technology for clean-up of specific metal(loid)s are demonstrated in Table 7.



3.8.1 Phytoextraction

It is a method in which plants absorb, translocate, and store metal(loid)s in their below-ground and above-ground parts. The plants are then either burned or composted to recover the metal(loid)s. If plants are burned, the ash essentially is discarded in a hazardous waste landfill (Sarwar et al., 2017; Lee et al., 2021). Benavides et al. (2021) evaluated Cd accumulating species: *Helianthus annuus*, *Brassica napus*, and *Chrysopogon zizanioides*. The plants were cultivated in two pot trials, each with a distinct Cd-amended growth medium: (sand + perlite) and natural soil. The total Cd and Cd absorption in shoot biomass augmented linearly with increasing levels of additional Cd in both studies. Plant total Cd was highest in *Brassica napus*, whereas Cd absorption in shoot biomass was highest in *Helianthus annuus*. Jacobs et al. (2018) used *Nocca caerulea* to remediate Zn in the field and demonstrated that the concentration of Zn in the plant's leaves exceeded 300 g Cd ha⁻¹ in 2 months. Fourati et al. (2016) removed Ni using *Sesuvium portulacastrum* by phytoextraction and showed that Ni was accumulated up to 1,050 µg g⁻¹ dry weight in the shoots of the selected plant. Herzig et al. (2014) conducted a Zn phytoextraction study using tobacco (*Nicotiana tabacum*) and sunflower (*Helianthus annuus*). The experiment was carried out for 5 years. The findings demonstrated that both plants exhibited good phytoextraction efficiency for Zn. The concentration of Zn was easily reduced by 45–70% in soil. Macci et al. (2013) evaluated the clean-up of a contaminated industrial region using a combination of metal(loid)s, hydrocarbons, and

polychlorinated biphenyls. *Populus sp.*, *Paulownia tomentosa*, and *Cytisus scoparius* were planted among naturally occurring plants with the addition of horse manure. The vegetation of *Populus sp.*, *Paulownia tomentosa*, and *Cytisus scoparius* reduced pollution by up to 35, 40, and 70% for metal (loid)s, hydrocarbons, and polychlorinated biphenyls (PCBs), respectively in 2 years. Tlustoś et al. (2006) conducted a phytoextraction experiment for As, Cd, Pb, and Zn using *Melilotus alba*, *Trifolium Pratense*, *Malva verticillata*, *Carthamus tinctorius*, and *Cannabis sativa*. The findings showed that the selected plants efficiently removed As, Cd, Pb, and Zn, and the highest efficiency was demonstrated by *Carthamus tinctorius*.

3.8.2 Rhizofiltration/Rhizodegradation

Rhizofiltration is the adsorption or precipitation of metal (loid)s onto plant roots. This technique is employed to clean the contaminated water rather than soil (Subba Rao et al., 2022). The plants are grown with roots immersed in water. The contaminated water is delivered to the plants, or the plants are put in the contaminated region, when the roots absorb the water and pollutants dissolved in it, plants are collected (Tiwari et al., 2018). Kumar and Fulekar (2022) demonstrated the rhizoremediation capability of *Pennisetum pedicellatum* for Cd removal in a pot culture experiment and the findings indicated that the selected plant species was effectively removed 83% of Cd within 2 months. Han et al. (2021) used uranium-polluted water and *Lactuca sativa*, *Brassica campestris L.*, *Raphanus sativus L.*, and

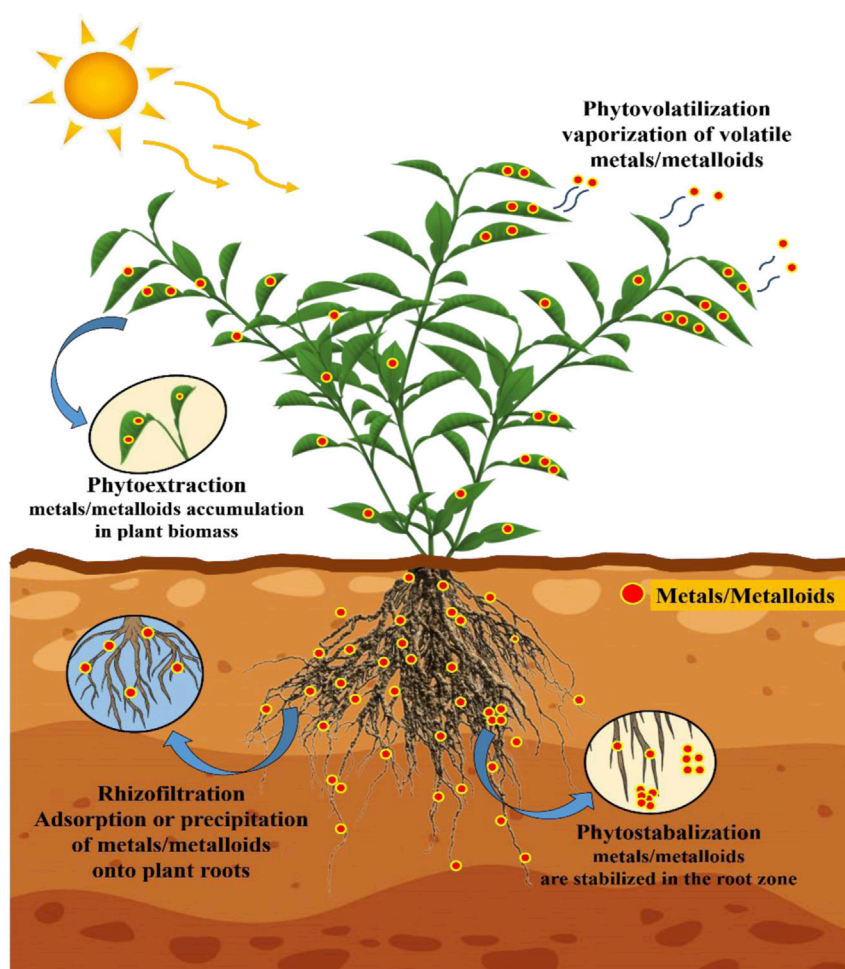
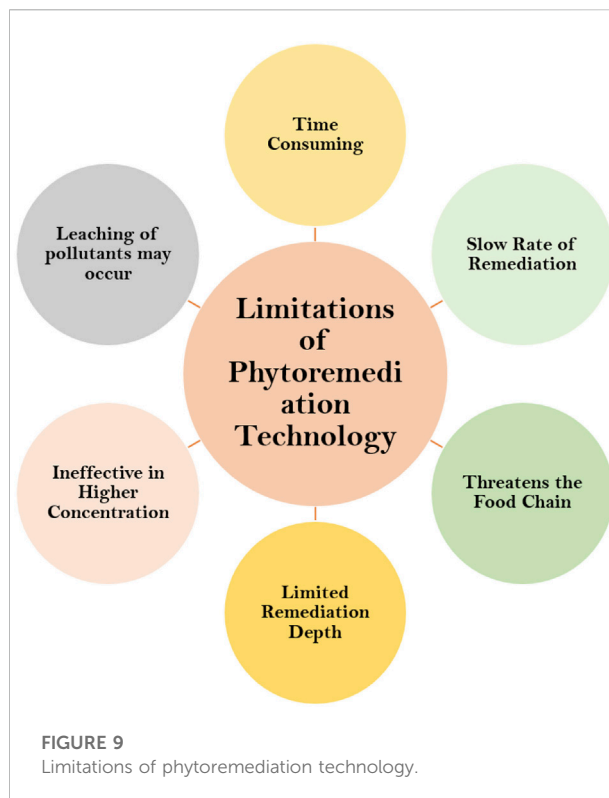
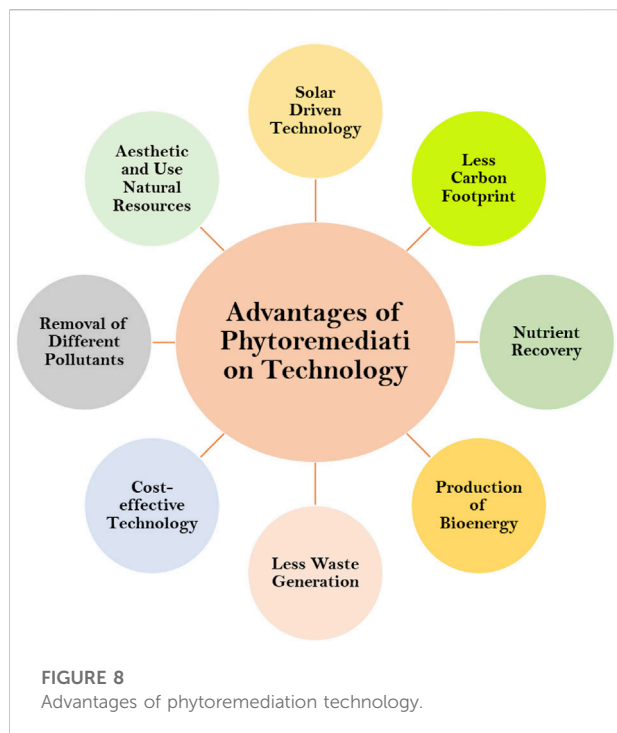


FIGURE 7
Schematic mechanism of phytoremediation technology.

Oenanthe javanica in a rhizofiltration study. The findings showed that as the U concentration in the groundwater increases, so does in the plant roots. Kodituwakku and Yatawara (2020) used *Eichhornia crassipes*, *Salvinia molesta*, and *Pistia stratiotes* to eliminate Cu, Cr, Cd, Ni, and Zn from industrial sludge. The findings indicated that *S. molesta* exhibited the highest reductions of Zn (36.0%), Fe (26.6%), Cu (32.6%), Cr (58.6%), and Ni, (26.9%) whereas *P. stratiotes* and *E. crassipes*, respectively, displayed the highest Cd (27.1%) and Pb (42.4%) reductions. Yang et al. (2015) demonstrated that metals like U and Cs were efficiently removed from the groundwater using *Phaseolus vulgaris*. Oustriere et al. (2017) specified that the *Arundo donax* is a proficient candidate to remove Cu from the constructed wetlands using the rhizofiltration technique. Vera Tomé et al. (2008) removed U and Ra (226) using sunflower (*Helianthus annuus*) and they reported that the rhizofiltration process was responsible for the elimination of metals. They reported 50 % and 70% of U and Ra (226) removal after 2 days, respectively.

3.8.3 Phytostabilization

In this technique, plants immobilize contaminants in soil and water by root absorption, accumulation, adsorption, or precipitation inside the root zone of the plants. This technique decreases pollutant mobility and inhibits relocation to water or air, as well as bioavailability for entrance into the food chain (Radziemska et al., 2017). This method may be applied to restore a vegetative cover in areas where natural vegetation has been lost owing to high metal(loid)s concentrations. Metal(loid)s-tolerant plants are utilized to decrease the possibility of pollutants movement by wind erosion and transfer of surface soils, as well as soil contamination seeping into groundwater (Shackira and Puthur, 2019). Sarath et al. (2022) attempted a phytostabilization experiment to remove As by *Acanthus ilicifolius* L. and described that this plant species to variable concentrations of As is the result of morpho-physiological and anatomical characteristics, which make the plant favourable for As removal, particularly in wetlands. Mataruga et al. (2020) assessed *Salix alba*, *Juglans regia*, and



Populus nigra for the biomonitoring of trace elements in the Sava River. The concentrations of As, Cd, Cr, Cu, Ni, Pb, and Zn were analyzed in the soils, roots, and leaves of plants. The findings demonstrated that *Salix alba* is a beneficial plant species for the phytostabilization of Cd and Cu. Zgorelec et al. (2020) determined the removal potential of *Miscanthus × giganteus* (MxG) for Cd and Hg. The concentrations of Cd (0, 10, and 100 mg kg⁻¹ soil) and Hg (0, 2, and 20 mg kg⁻¹ soil) were supplemented to the soil. MxG was able to accumulate (293.8 µg Cd and 4.7 µg Hg) in shoots. The findings suggested that *Miscanthus × giganteus* (MxG) is a potential species for phytostabilization on soils polluted with Cd and Hg. Bacchetta et al. (2018) specified that the uptake of Zn, Cd, and Pb was limited mainly in the roots of *Helichrysum microphyllum* which is appropriate for the phytostabilization process. Al Chami et al. (2015) evaluated the removal efficiency of *Sorghum bicolor* and *Carthamus tinctorius* for Ni, Pb, and Zn. The findings specified that both the species were capable to accumulate these elements in their roots.

3.8.4 Phytovolatilization

In this technique, plants absorb contaminants and transform them into less toxic volatile forms. The contaminants are absorbed by the roots, transferred to the shoot, then volatilized in the atmosphere *via* the stomata of leaves (Nedjimi, 2021). Phytovolatilization has been applied to remove volatile elements such as Hg and Se (Cristaldi et al., 2017). Mahar et al. (2016) stated that this technology may be implemented to remove different organic contaminants and metal(loid)s such as Se, As, and Hg from the environment. Guarino et al. (2020)

described that *Arundo donax* has the potential to volatilize more than 50% of As aided by *Stenotrophomonas maltophilia* and *Rhizobacterium* sp. Moreno et al. (2008) described Hg removal using *Brassica juncea* (L.) grown in hydroponic conditions with Hg concentrations of 0–10 mg/L. The findings concluded that *Brassica juncea* has the potential to remove Hg up to 95% by phytovolatilization. The volatilization of Hg mainly happened from the roots in the Hg (0) vapour form.

3.9 Advantages and limitations of phytoremediation technology

3.9.1 Advantages

The phytoremediation technology is efficient with lots of benefits (Figure 8).

1. Phytoremediation is less expensive since it does not need the purchase of large equipment.
2. Planting trees on contaminated sites make these areas more attractive.
3. Plants can be grown quickly and simply with little effort, and they can also be checked effortlessly.
4. The precious metal(loid)s can be recovered and reused.
5. The phytoremediation technology uses natural organisms to protect the environment, thus it is potentially the least destructive technology.

6. It protects the topsoil and thus maintains soil fertility.
7. It increases the plant phytochemicals and improves the health of soil and yield.

3.9.2 Limitations of phytoremediation

Phytoremediation is simple to use and cost-efficient, however, it does have significant technical limitations (Figure 9).

1. Phytoremediation just relocates hazardous metal (loid)s rather than complete removal.
2. The zone and depth engaged by the roots are the only areas where phytoremediation may take place.
3. A long-term commitment is required due to the slow growth of the plants.
4. It's impossible to prevent metal(loid)s from seeping into groundwater using this technique.
5. To be accessible to the roots, the contaminant must be present inside the root zone.
6. The pollutants may transfer to the food chain during phytoremediation.
7. The phytoremediation technique is less efficient for the higher concentration of contaminants.

3.10 Future prospects of phytoremediation technology

Phytoremediation is the most favourable technology for the eco-restoration of contaminated environments, however, more studies and analyses are necessary to develop our understanding of effective phytoremediation of metal(loid)s. More study into metal(loid)s remediation would contribute insights into phytotoxicity limits, and genetic engineering may enable plants to withstand larger metal(loid)s concentrations. In field trials, it is essential to look for new approaches to understand the processes, metabolites, and genes employing cutting-edge omics techniques. Further study in the following areas looks to be worthwhile in the future to secure further advantages.

- i. Identification of potential plants containing compounds that may prevent herbivores, followed by transformation of such plants with altered or increased metal tolerance capacities; such a system will aid in avoiding metal transmission to the food chain.
- ii. Transgenic phytoremediation experiments must be applied in the contaminated areas to deal with the metal (loid)s as well as other types of pollutants.
- iii. A multigene technique that involves the parallel delivery of numerous genes into eligible candidate plants could aid in the removal of pollutants.
- iv. Cropping system identification with targeting elements and site-based phytoremediation.
- v. Farmers, local populations, academics, industrial sectors, and environmental specialists may contribute to the success and

dependability of phytoremediation through teaching initiatives, ensuring the long-term sustainability of this environmentally beneficial green technology.

4 Conclusion

The presence of metal(loid)s in the environment is a challenging issue associated with ecological and human health and their clean-up is a global concern that needs to be addressed. The understanding of metal(loid)s contamination concerning their recent global scenario, sources, the necessities for removal, and impacts on human health and the ecosystem are very important to predict the future strategies to deal with this problem. According to the findings, anthropogenic activities have considerably contributed to excessive quantities of metal(loid)s discharge into the environment. Various technologies to eliminate these harmful metal(loid)s from the environment are significant and functional according to the need, types, and conditions of remediation sites. However, the search for better clean-up technologies either in the combination or modification of existing ones or new technologies with cutting-edge scientific advancements is the need of the hour. Selective technologies like phytoremediation, ion exchange, membrane filtration, and adsorption, all have benefits and drawbacks when it comes to metal(loid)s removal from the environment. A systematic understanding of metal (loid)s sources, their chemistry, and possible hazard to the ecosystem and humans are required to choose a proficient clean-up technology and its proper management to make better strategies and sustainable policies for the future.

Author contributions

PK: Methodology, Writing- Original Draft. AG: Supervision. MA: Conceptualization, Methodology, Writing- Original Draft. VY: Writing- Original Draft, Formal analysis. SS: Formal analysis, Resources, Writing- Review, and Editing. VD: Writing- Original Draft, Formal analysis. MA: Writing- Original Draft, Formal analysis. KY: Writing- Original Draft, Formal analysis. SP: Data curation, Formal analysis. PM: Formal analysis, Writing- Review, and Editing. MC-P: Formal analysis, Writing- Review, and Editing. YA: Formal analysis, Writing- Review, and Editing. B-HJ: Supervision, Formal analysis.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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