Cleaner technologies to combat heavy metal toxicity

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Graphical abstract
Abstract

Heavy metals frequently occur as silent poisons present in our daily diet, the environment we live and the products we use, leaving us victims to various associated drastic health and ecological bad effects even in meagre quantities. The prevalence of heavy metals can be traced from children’s toys, electronic goods, industrial effluents, pesticide preparation, and even in drinking water in some instances; necessitating methods to remediate them. The current review discusses the various physicochemical and biological methods employed to tackle the problem of heavy metal pollution. Apart from the conventional methods following the principles of adsorption, precipitation, coagulation, and various separation techniques, the advancements made in the directions of biological heavy metal detoxification using microbes, plants, algae have been critically analyzed to identify the specific utility of different agents for specific heavy metal removal. The review paper is a nutshell of different heavy metal remediation strategies, their merits, demerits, and modifications done to alleviate process of heavy metal pollution.

Keywords: Heavy metal; Biosorption; Ultrafiltration; Nanoremediation; Phytoremediation; Microbe
1. Introduction

The United Nations in 2019 proclaimed the period of 2021-2030 to target Ecosystem Restoration and worldwide attempts are directed to this Nobel cause (https://www.unenvironment.org/news-and-stories/story/when-we-protect-nature-nature-protects-us). A multifaceted approach involving the restoration of habitats (Jones et al., 2018), remediation of toxic wastes (Piccolo et al., 2021; Surbeck and Kuo, 2021), prevention of pollution (Zhu et al., 2021), effective solutions to xenobiotic removal (Liu et al., 2021b), and exploration of alternate technologies instead of nature hampering processes are devised to combat the aftermaths of different xenobiotics. Among the various xenobiotics, heavy metals represent a group of silent metallic pollutants, leaving back chronic health effects to living forms (Jan et al., 2015), drastic changes in the soil, sediments, air, and associated ecological niches (Daniel et al., 2021). Heavy metals represent a group of indestructible poisons which accumulate in the food chain and its analysis has gained much attention since 1870’s (Wanklyn and Chapman, 1870). These metals so-called heavy for their densities greater than five; are also known as trace elements due to their low concentration permitted in the body to avoid toxicity (Singh et al., 2011).

Various anthropogenic activities contribute to the heavy metal pollution, of which mining weighs as a major contributory factor leaving back a diverse range of heavy metals (Sun et al., 2018). Apart from this, activities of chemical industries (Gabarrón et al., 2017), smelting of various metals, nuclear plants, fertilizers, pesticides, electronic wastes, etc have aggravated the burden of heavy metal contamination. A shift in the cause of heavy metal pollution from manufacturing and mining to contributory factors such as rock weathering and waste exudates has been observed these years (Zhou et al., 2020).
Instances of intentional heavy metal poisoning in ancient history as well as cases of accidental heavy metal exposure are prevalent contemporarily (Grimalt et al., 1999; Liu et al., 2021a; Waldron, 1988). The essential heavy metals (Cu, Cr, Co, Fe, Zn) in high concentrations, as well as nonessential heavy metals (Al, Pb, Cd) in low concentrations are to be taken seriously if they exceed the permissible limits (Kfle et al., 2020). Studies indicate that such permissible limits of heavy metal concentrations (mg/L) in aquatic bodies Hg-0.002, Cd-0.05, Pb-0.015, Cr-0.01, and Ag 0.05 are often not met in many situations (Jaishankar et al., 2014). The trend of heavy pollution has changed from single to mixed metal pollutants over years (1972 to 2017) with heavy metals in waters above the permissible threshold levels globally (Zhou et al., 2020). Heavy metals such as lead, mercury, copper, arsenic, cadmium, chromium are predominantly considered toxic and need to be treated and abated from nature.

Mostly heavy metals are persistent, non-biodegradable in nature, which can’t be destroyed completely. The presence of heavy metals from various sources transports down via food chains to humans as well as animal bodies (Ali et al., 2014; Siddiquee et al., 2015). Comparative analysis on different human populations indicated that low-level exposure of heavy metals such as cadmium, lead, and mercury drastically affected the reproductive ability of human males (Wirth and Mijal, 2010). Heavy metals become toxic and get deposited in the cells when they are not being metabolized by the natural process of digestion of the human body (Engwa et al., 2019). The itinerant nature of heavy metals, along with their role in disrupting the proteins leads to disruption of balanced metabolism and functioning of organs such as the brain, liver, kidney etc (Jaishankar et al., 2014). Moreover, chronic exposure to these metals causes health and environmental dilemmas. The major health hazard caused by long-term exposure to these metals is proven to cause allergies, cancer and other health problems (Yuan et al., 2016). Apart from this, heavy metal toxicity simultaneously adds on to
more misery by the development of antibiotic resistance in resident microbes of water bodies (Komijani et al., 2021).

The abatement of these heavy metals by natural as well as human interventions from the polluted environment thereby converting them to life supporting healthy niches have been a subject of supreme importance (Vardhan et al., 2019). An apropos strategy is essential for the removal of these toxic metals both from the human body as well as the environment. The entire cycle of heavy metal treatment is effective when combinatorial approaches utilizing physicochemical and biological techniques are adopted sequentially to get the best results (Khalid et al., 2017).

This mini-review outlays the different physical and biological methods adopted in heavy metal removal from contaminated areas. The choice of the method for heavy metal removal varies for different heavy metals, type of sample to be processed (for instance, soil or water), severity of damage caused by heavy metal and the urgency of its treatment. The current review provides a better understanding of different heavy metal detoxification strategies, their advantages, drawbacks and advancements made in the field of heavy metal detoxification, to pave the way of further research and developments.

2. Heavy metal Removal

Heavy metal toxicity can be removed by several methods that are adopted by the current world, such as physical, chemical, and biological methods. Among these, physical methods are more gained attention due to the ease of use and cost-effectiveness. Chemical methods involve the addition of chemical agents which precipitate the inorganic heavy metals thereafter to be removed by downstream treatment involving various strategies (Barakat, 2011).
2.1. Physical methods for the removal of heavy metal

The treatment strategies of heavy contaminated soil and water regardless of the difference in their physical state follow similar principles of treatment with a common aim of heavy metal removal. However, the choice of the method relies on the economic and technical feasibility quite often. Most predominantly the methods of industrial heavy metal removal involve the treatment of industrial wastewater than soil, thus more developments are made in that direction. Table 1 depicts some of the physical methods of heavy metal removal.

2.1.1 Adsorption

Physical methods such as adsorption are found to stand out as the best method for heavy pollution removal over other methods such as membrane filtration, ion exchange, and electrodialysis due to their less negative effects, environmental beneficiary effects as per life cycle analysis (Nazaripour et al., 2021). The use of cost-effective agricultural waste based adsorbents such as rice husk, sawdust, Groundnut husk, wheat bran, etc following use of modifying agents viz, sodium hydroxide, sodium-bicarbonate, formaldehyde, etc (Sharma et al., 2016) has been practiced. Such methods are noted for their effectiveness over lower or higher contaminate concentrations, ability to alter the selectivity of adsorbate by using suitable components via the modifying agents, and its economic feasibility. The use of biochar (Qiu et al., 2021) and chemically modified chitosan with an 80% rate of removal (Sheth et al., 2021) are some yet other instances of adsorption. The effectiveness of phosphate modified magnetite@ferrihydrite (Mag@Fh-P) in the specific removal of Cadmium from the soil as well as water, its cost-effectiveness, and easy separation adds to its advantages (Fu et al., 2021).
2.1.2. Soil Replacement

The techniques such as soil replacement involve the replacement of contaminated soil by non-contaminated soil can only be useful in the treatment of heavily polluted small areas of soil, requiring high expense for soil importing and limitations in its applicability in agricultural land as soil fertility is lost (Yao et al., 2012). Soil isolation technologies are designed in such a way that to prevent the off-site traveling of heavy metals prevent the contamination of groundwater resources. By these methods, contaminated sites are isolated with the help of other auxiliary engineering measures like subsurface barriers to restrict their flow to the natural resources (Bodocsi et al., 1995). The flow barriers are installed depending on the flow of water streams and the depth is limited to 30 ft. The materials which are used as sub-surface barriers include grout curtains, slurry walls, and sheet piles.

2.1.3. Vitrification

In vitrification, the contaminated site is subjected to high-temperature treatment so that the mobility of the heavy metals inside the soil is reduced. As a result of this process, vitreous materials are formed and the volatilized metal species are collected for further treatment or disposal (Mallampati et al., 2015). In the case of soils contaminated with inorganic and organic contaminants, in situ vitrification process can be done by passing an electric current through the vertically inserted array of electrodes. Processes like excavation, mixing, pre-treatment, melting feeding, and casting of the melted product are required in the case of ex situ vitrification. The process of vitrification finds more relevance in the treatment and further immobilization of radioactive substances thereby reducing their spread to the environment (Ojovan et al., 2019). Also, the successful application of this technique depends on the conductivity and alkali content of the soil (Buelt and Thompson, 1992). Though this remediation technique is cost-effective only if it is applied to small sites polluted with heavy
metals; its utility is valued when highly dangerous heavy metals like radioactive substances have to be immediately dealt without any further delay.

2.1.4. Electrokinetic Remediation

Electrokinetic remediation is operated on the principle of the electric field gradient. In this process, an electrolytic tank containing the contaminated soils is placed in between the electric field gradient. By electrophoresis, electro-migration happens and the contaminated soil gets filtered out (Yao et al., 2012). Several chemicals, biological, and nanofiber remediation techniques are also used in combination with electrokinetic remediation (Khalid et al., 2017). To increase the efficiency of this process the proper use of an electrolyte such as distilled water or organic acids are essential. This technique operates well for solids having low permeability. The process is relatively effective and easy to install when compared with other methods for the removal of heavy metals from the soils. Fluctuation in soil pH is a limiting factor for direct electrokinetic remediation. The principles of electrocoagulation and electro-oxidation find use in heavy metal treatment strategies of companies such as RTECo (Heavy Metal Removal Plant | RT ECO / ETP), to generate eco-friendly reusable water from effluents meeting the environmental regulations (https://www.rteco.in/all-products).

2.1.5. Particle Trapping System

Pollutants from the contaminated water are physically removed using a particle-trapping system (PTS) (Khoei et al., 2018). This system consists of two containers of dimensions 30 x 20 x 25 cm, partitioned into three parts which include (1) water entrance (2) particle- trapping part (PTP) containing PVC-based straws, and (3) pumping part. Through the water entrance, the contaminated water is passed and the same reach the PTP added with the stock solution of Ar and other pollutants. After passing the PTP, the contaminated water is reached the
pumping part from where it is flooded back to the first part. In this technique, particles with a
diameter of more or less than 50 µg can be removed.

2.1.6. Nanoremediation

Another emerging application that came across for treating heavy metals is the use of
nanomaterial (Chen et al., 2016). Nanoremediation is commonly used for treating
wastewaters and it is being considered as one of the green technologies (Bardos et al., 2018).
Nanoremediation plays a versatile role in heavy metal detoxification with some candidates
such as ferromagnetites aiding the selective removal of heavy metals from different niches of
soil, air, water (Carlos et al., 2013) as well as from plants (Konate et al., 2017). Nanofibers,
Carbon-based nanoparticles, Photocatalytic NMs are the commonly used strategies along
with the electrochemical process. Mainly used nanomaterial involves iron oxide
nanomaterial. Also, nano-sized semiconductor materials of ZnO, TiO₂, etc., are used. The
type of nanomaterial majorly depends on the process involved.

The high efficiency of amorphous calcium carbonate nanoparticles stabilized in poly(acrylic)
acid to deal with heavy metals such as Pb, Cd²⁺, Pb²⁺, Cr³⁺, Ni²⁺ ions and even radioactive
Eu³⁺ ions noteworthy for its role in water treatment (Cai et al., 2010). The use of graphene
oxide nanoparticles proved promising in the immobilization of heavy metals such as Cu,Pb,
and Cd and zerovalent iron nanoparticles were efficient in As and Pb immobilization from
soil (Baragaño et al., 2020). A close evaluation indicates that a selective preference was
exhibited by different nanoparticles in their potential to immobilize heavy metals. This also
suggests the possibility of using different nanoparticles in combination for the removal of a
multitude of heavy metals.
The combinatorial use of nanoparticles along with other modes such as phytoremediation has gained momentum due to the increased rate of pollutant decontamination and regeneration (Chen et al., 2021). Even amidst the instances of heavy metal and nanoparticle induced toxicity in plants, we come across examples where nanoparticles are used to reduce the heavy metal toxicity in plants (Mustafa and Komatsu, 2016; Venkatachalam et al., 2017). Similar cases of nanoparticle aided heavy metal toxicity reduction can also be seen in other life forms. TiO$_2$ nanoparticles raise therapeutic significance by reversing the ill effects of Pb toxicity in lung epithelial (E549) cells (Ahamed et al., 2019) and citrate coated silver nanoparticles were found to be promising in reducing the ill effect of heavy metal bioaccumulation in *Daphnia magna* (Kim et al., 2016). Moreover, it can be seen that the use of polyhydroxybutyrate-carbon nanoparticles in heavy metal remediation could aid to need a short treatment time of 1.5 hrs at a dosage of 20 mg of heavy metals, at pH around 5.5 (Bankole et al., 2019).

### 2.2. Chemical methods

Chemical methods of heavy metal removal follow the principle of chemical precipitation, chelation, coagulation, and consequent separation by any of various methods such as ultrafiltration, electrodialysis, membrane filtration, etc. (Charerntanyarak, 1999). Conventionally the electroplating effluents rich in heavy metals are treated with lime or calcium hydroxide which results in an alkaline pH thereby precipitating the heavy metals to their insoluble hydroxide derivatives (Kurniawan et al., 2006). Chemical precipitation has also been carried out using various synthetic agents such as 1,3-benzenediamidoethanethiol dianion (BDET, known commercially as MetX) (Matlock et al., 2002), hydroxide- sulfide precipitation (Cort, 2007) and synthetic magnesium hydroxycarbonate(Zhang and Duan,
especially in the treatment of industrial wastewater yielding hydroxide or carbonate or sulfide precipitates.

Coagulants such as alum, ferrous sulphate, ferric chloride etc aid in aggregation and flocculation of repelled heavy metal precipitates derivatives thereby promoting their further separation (Johnson et al., 2008). The binding of heavy metal derivatives on ion-exchange chelators would further aid in their removal from chemically treated water or soil (Diarra et al., 2021). Prominent biologically used chelators include Calcium Disodium Ethylenediamine Tetraacetic Acid, British Anti Lewisite (BAL), Sodium 2, 3 Dimercaptopropane-l-Sulphonate (DMPS), Monoisoamyl DMSA (MiADMSA), Deferiprone (L1), etc(Flora and Pachauri, 2010).

The integration of the membrane ultrafiltration (UF) process with chemical coagulation is an innovative method used to separate pollutants. The use of polyethersulfone (PES) membrane for the simultaneous removal of Co$^{2+}$ ions, Cd$^{2+}$ ions, and Pb$^{2+}$ ions (Ahmed et al., 2021), use of electroanalytic techniques (Altaf et al., 2021), low-cost plant based flocculants such as Taccaleontopetaloides are yet some advancements in the chemical treatment of heavy metals (Mohd Makhtar et al., 2021).

Commercialized water treatment units to remove heavy metals such as chromium, Zinc, Nickel, Copper, etc are reported to follow chemical precipitation and dewatering filtration experiments (https://www.alarcorp.com/metals/). Chemical precipitation methods are advantageous due to their easy operation requiring no instrumentation and simplicity; however, the need for a large amount of chemicals to recover heavy metals to their permissible limits and the formation of sludge is counted as its disadvantages (Barakat, 2011).
The use of ionic liquids in the remediation of heavy metals from soil has been researched owing to its wider range of dissolution, better solubility and low vapour pressure (Jia and Liu, 2021). Yet another strategy to heavy metal removal from fine-sized particles like contaminated soil is by washing with citric acid and ferric chloride in slurry reactors achieving approximately 90% recovery of different heavy metals (Shi et al., 2020). A comparative study on the efficiency of heavy metal removal by washing sand indicated that ferric nitrate was a better candidate than citric acid (Zhihong Guo, 2021). Thus the chemical treatment of both heavy metals contaminated soil or water is found effective, regardless of the concerns of extensive chemicals needed to recover heavy metals.

2.3. Biosorption

The advantage of biosorption is that it represents an effective and economically feasible method to deal with large volumes of effluents with a low concentration of biosorbent without any toxic secondary product generation (Abbas et al., 2014). The short time operation is another added advantage of this process. Important mechanisms that are involved in the biosorption process are complexation, chelation, coordination, ion exchange, precipitation, reduction, etc.

2.3.1. Microbes

Heavy metals are dealt with using a wide range of microbes using either biosorption or bioaccumulation principles. The former involves the physical adsorption of heavy metals on the surfaces of biological agents due to the physicochemical attraction, complexation, and chelation (Torres, 2020). Biosorption thus is greatly influenced by parameters such as pH of the medium and both viable and dead microbes can do the purpose of heavy metal adsorption (Chatterjee et al., 2010). Another advantage of biosorption is that the heavy metals can be
recovered from the biosorbent by altering the pH to lower levels destabilizing the metal from the biosorbent (Lata et al., 2015). The extracellular polysaccharides of some microbes, for instance, irreversibly attached to silica columns were found to be 99.9% efficient in Cu$^{2+}$ and Pb$^{2+}$ adsorption whereas, it had a metal recovery percentage of 86% for Cu$^{2+}$ and 90% for Pb$^{2+}$ (Ajao et al., 2020). Dead cells of *Pseudomonas putida* in agar beads were found to be effective in Cu ion removals with 60% removal efficiency for 10 successive cycles when fixed-bed columns were set (Meringer et al., 2021). The use of dead cells in heavy metal remediation of effluents also nullifies the concerns of required microbial treatment in post-treated effluents. Moreover, in other studies conducted using MgO nanoparticles in heavy metal removal, it was also noted that pathogenic *Escherichia coli* were also killed during the treatment of wastewater (Cai et al., 2017). Table 2 depicts an outline of some microbial agents used in heavy metal removal.

Bioaccumulation on other hand, involves the use of inherent microbial proteins that sequester and utilize bioaccumulated metals in various metabolic processes of the microbial cell (Diep et al., 2018). Metal binding proteins of some microbes help them to bypass the toxicity of heavy metals and develop microbial tolerance to such metals (Sharma et al., 2021). Metals are transported across the lipid membrane using specific transport proteins and in cases of metal resistance of mercury as well as arsenic the involvement of reductase proteins in the development of resistance is noted (Hao et al., 2020). Such heavy metal-resistant bacteria aid in the remediation of heavy metals by bioaccumulating them in the microbial cell (Ahemad and Malik, 2011). The use of heavy metal resistant microbial consortium in sorghum fields prevented the retention of heavy metals in sorghum grown in that environment; thereby specifying the relevance of microbial bioaccumulation of heavy metals (Abou-Aly et al., 2021).
Various biological products such as cyanobacteria exopolysaccharides aid in the absorption of a wide variety of heavy metals. The complex nature of cyanobacteria exopolysaccharides with the presence of repeating units of different sugars in high concentrations, metallothionein based proteins, pyruvic acid moieties, uronic acids, lipids, and DNA aid in the selection absorption of heavy metals and remediation (Yadav et al., 2021). Novel strategies to develop genetically engineered microbe of *E. coli* with phytoalexin gene expressed in it and thereby aid in heavy metal bioaccumulation have also been attempted (Bae et al., 2000). The combination of immobilization techniques with different metals utilizing microbes could also aid to set various reusable cycles of heavy metal detoxification processes (Srivastava and Gupta, 2021).

*Trichoderma* derived harzianic acid are also found to be promising in heavy metal removal (Tommaso et al., 2021). The increased heavy metal tolerance and remediatory role of fungi are found to be associated with the presence of enzymes such as cytochrome P450 monooxygenases and glutathione transferases (Goutam et al., 2021). The use of biogenic sulfide precipitation using Sulphate Reducing bacteria are found to be noteworthy for removal of heavy metals even in low concentrations using low cost in anaerobic conditions of microbial growth (Kumar et al., 2021). Regardless of all the benefits of microbial mediated heavy metal recovery, the fact that excess heavy metals beyond a critical level could also be toxic to microbes (Inobeme, 2021) and thus the effectiveness of microbial candidates in heavy metal removal will be realistic only if the treating effluent has a treatable limit of heavy metal. In such cases, cleaner technologies involving a combinatorial approach of phytomining methods along with microbes will be a wise strategy for heavy metal removal (Alves et al., 2021).
2.3.2. Phytoremediation

Phytoremediation serves as an effective alternative to addressing heavy metal pollution in large areas of soil particularly in agricultural fields where the use of chemical treatment or other physical methods of heavy metal removal is not cost-effective (Nedjimi, 2021). The advantages such as applicability in *ex situ* and *in situ* treatment, low cost, utility in areas not requiring excavation, metal recovery post phytomining as well as its least harmful nature have greatly promoted plant-mediated heavy metal remediation (Awa and Hadibarata, 2020)(Anoopkumar et al., 2020). However, concerns do exist in the entry of heavy metals into the food chain (Farraji et al., 2016), and its noted that rice varieties witness the accumulation of heavy metals such as cadmium (Cd), arsenic (As), and lead (Pb) into them (Zakaria et al., 2021). The use of less heavy metal accumulating agricultural cultivars and thereby exclude the heavy metals from soils to enter cultivar varieties in highly heavy metal contaminated agricultural lands has also gained momentum (Wang et al., 2021c). The use of ornamental plants in heavy metal remediation is considered advantageous over agricultural crops as the former is safer as there is less chance of bioaccumulation (Khan et al., 2021; Madanan et al., 2021). Moreover, the heavy metal remediated ornamental plant can still be counted for its aesthetic importance and source of value-derived products such as perfumes, essential oils.

A wide range of plants ranging from hyperaccumulating varieties such as wetland plants *Acorus calamus* (Sarma, 2011; Wang et al., 2021a), sandy soil located *Pinus sylvestris L.* (Çomaklı and Bingöl, 2021), desert located *Prosopis laevigata* (Buendía-González et al., 2010) have been used to remove heavy metals as indicated in Table 3. In a case study reported in India plant varieties of switch grass were quite effective in the removal of Pb and Cd (Arora et al., 2016). Plant varieties such as *Trifolium repens* L. are effective heavy metal...
quenchers of both cations and anions (Lin et al., 2021). A comparative analysis of plant cortex for heavy metal detoxification indicated that lemon and orange cortex was best for Pb and Cu removal, whereas banana cortex was effective for Cd removal (Kelly-Vargas et al., 2012).

Plant-based heavy metal remediation has been widely used to remove heavy metals from soil using the principles of phytovolatilization (volatizing heavy metals to atmosphere), phytodegradation (break down of heavy metals by enzymes), phytofiltration (trapping of metals from water), phytoextraction (uptake and storing in shoots), phytodesalination (use of halophytic plants), rhizodegradation (uptake and degradation of metals using microbes of rhizosphere) and phytostabilization (root assisted limiting of metal mobility) as depicted in Fig 1 (Manousaki and Kalogerakis, 2011; Mitra et al., 2021). Plants are noted for their metal remediation problems owing to the synthesis of metal-chelating proteins such as metallothionenin and phytoalexins (Cobbett, 2000). The mechanism of heavy metal detoxification mainly involves its chelation using ligands and its subsequent entrapment in remote cavities. Such ligands include a great number of candidates ranging from organic acids (citrate, malate etc), amino acids such as histidine etc.

The association of endosymbiotic microbes and their secondary metabolites do contribute to the heavy metal detoxification of many plants are also note as in the case of plant association with arbuscular fungi (Heggo et al., 1990; Miransari, 2017). The association of microbe-derived sophorolipids in enhancing the heavy metal remediation by plants is yet another instance of microbial secondary metabolite-assisted heavy metal desorption (Shah and Daverey, 2021). Nanoparticles in some cases are found to increase the heavy metal absorption in plants that had previously identified as prospective candidates for heavy metal remediation (Zand et al., 2020). In addition to various methods, it can be noted that anaerobic
digestion using different organic substrates such as plant-based rice straw displayed more heavy metal retention ability in contrast to animal-based manure, thereby pointing out the role of plant derivatives in heavy metal remediation (Zheng et al., 2021).

2.3.3. Algae

Phycoremediation serves to be an effective heavy metal remediation strategy utilizing brown algae, red algae, and green algae either in the living or dead stage (Nazal, 2019). The algal population also follows the principle of biosorption to remove heavy metals from contaminated water (Rangabhashiyam and Balasubramanian, 2019). The cell wall composition of algae inherently contains various chemical groups viz. amino and carboxy, imidazole, phosphate, phenolic, thioether, and sulfhydryl moieties that selectively bind the heavy metals onto them (Spain et al., 2021). The algae can serve as anionic and cationic exchangers, chelating agents, pH-based precipitating agents, and form complexes by electrostatic or covalent interactions to remove heavy metals from effluents (Nazal, 2019). Apart from the living algal forms, the extracts of various brown algae containing bioactive polysaccharides and their butanedioic anhydride derivatives are found to be effective in heavy metal bioadsorption (Li et al., 2020). A concise review of the various aspects of algal heavy metal remediation has been noted (Rangabhashiyam and Balasubramanian, 2019).

Various studies on algal heavy metal remediation indicate that different algae possess different efficiency for their removal. Microalgae *Chlorella kessleri* showed a heavy metal efficiency at the order of Pb (II) > Co(II) > Cu(II) > Cd(II) > Cr(II) (Sultana et al., 2020). In another study, heavy metal removal by Duckweed (*Lemna minor*) and indigenous algal systems displayed that the removal of chromium alone from textile wastewater on post-treatment was possible, but these biosorbents were reluctant to heavy metals such as Pb, Cd, and Cu; indicating the need of other alternatives in their removal (Sekomo et al., 2012). A
comparative analysis of heavy metal utilization by different indigenous algal species of heavy metal polluted pond containing cyanobacteria, diatoms, green algae indicated that *Anabaena* was the most effective one followed by *Phormidium, Nostoc, Spirogyra*, etc (Kumari, 2021). Algal biomass including a consortium of *Chlorella* and *Phormidium* was capable of removing 50-90% of heavy metals in 9 days (Naaz et al., 2021). Regardless of the availability of different algae for heavy metal removal, standardization of single algae-based strategies cannot be made as different algae have different specificity for heavy metals as noted in Table 4.

Moreover, apart from the algae individually, modifications of algae as well as pre-treatment have been found to alter the heavy metal biosorption water. The combination of algae *Fucus vesiculosus* with biosorbents such as calcium alginate polyethyleneimine showed higher selectivity for Pb and Cu over Cd, Zn, and Ni (Demey et al., 2018). Composites of nonliving *Ulva fasciata* (U) with cellulose acetate-based polymeric membranes were found to be effective for Cd$^{2+}$ and Zn$^{2+}$ from aqueous solutions (Abdelhamid et al., 2021). The high specificity and doubling in the uptake of Cu from even aqueous solutions was achieved by the use of magnetized derivatives of biochar of waste macroalgae kelp, with magnetization aiding an additional advantage of easy separation of heavy metals (Son et al., 2018). The use of biochars derived by pyrolysis in oxygen-limited conditions of different organic wastes though practiced earlier, kelp and hijikia based biochars were found to be superior to pinewood sawdust-based biochars as noted in the above study.

Though the major bottleneck to algal heavy metal remediation mainly depends on its extraction methods which could involve physiochemical treatments such as heating, acid-base treatments, etc, and the beneficial, cost-effective, and selective heavy metals biosorption properties of algae outweighs the associated difficulties. The treatment of heavy metal
contaminated algal biomass yet another concern can be resolved by the process of thermal liquefaction in a high-temperature pressure reactor to recover the heavy metals from algae post-remediation treatment which yielded approximately 70% of heavy metal in the solid phase of the extract (Naaz et al., 2021).

3. Limitations and future scope

Different methods of heavy metal remediation have pros and cons as noted in Table 5 and the choice of a particular method depends on its economic utility, practical ease, ecological feasibility, timely removal and efficiency. The identification of the limitations of each technique and the efforts to improvise them could surely expand their future scope. The major concern of heavy metal detoxification by landfills is the re-localisation from one site to another rather than the complete removal and even after remediatory method the safety concerns raised by heavy metal raised to the adjoining environment and water bodies still remains (Boateng et al., 2019). In other words heavy metals are relocated from one site to another site using different methods with the common aim of reducing the toxicity associated with the heavy metal at the site of its occurrence. However, even toxic heavy metal laden soil could be converted to healthy soil by techniques of phytoremediation as well as supplementation of nutrients such as ferrous sulphate thereby enhancing the indigenous microbial flora (Anoopkumar et al., 2020; Sigua et al., 2016).

Chemical precipitation of heavy metals from waste water seems to be the widely used technique for concentrations above 1000mg/L, due to its ease of operation, fast results, inexpensive equipment requirement (Barakat, 2011). The high usage of chemicals, generation of heavy metal loaded sludge, low solubility of metals and methods to dispose such sludge are a major challenge that needs to be addressed (Renu et al., 2016). The use of appropriate strategies to immobilise such chemicals on sludge by techniques such as composting and
chemical immobilisation to prevent their leakage on further land application also need to be verified (Zhang et al., 2017). The use of chemical pyrolysis of sludge waste to obtain heavy metal leachate and their further adsorption to chitosan has also been noted to effectively remove heavy metals like Pb (Pietrelli et al., 2019). But concerns still exist as the chemical pyrolysis again demands the use of acid treatment with HCl or H₂SO₄, followed by metal precipitation from leachate.

Though the concept of adsorption of heavy metals using various agents has been studied, the success of every adsorptive agent depends on its adsorption capacity, reusability of the adsorbent and the ability to adsorb heavy metals at low concentrations (Czikkely et al., 2018). In such a scenario, the availability of nanoparticles and their composites with better adsorption capacities help to overcome the discrepancy associated with unmodified natural adsorbents (Soni et al., 2020). The activation of soft wood chips or biochars by ultrasound and alkali treatment enhanced the heavy metal removal by 22 times than nonactivated biochars, signifying how a simple modification could increase adsorptive ability of heavy metals in some cases (Peter et al., 2021). The use of still new adsorbents such as zeoliticimidazolate framework (ZIF-8) with better adsorption efficiencies could be promising in heavy metal removal from aqueous solutions in near future (Li et al., 2021).

The availability of biosorbents as well as their derivatives aid in providing eco-friendly solutions to heavy metal desorption in areas where chemical application or adsorbent use is not practical, however, the long duration of treatment required by them is a bottleneck to its wide use currently (Sameera et al., 2011). Molecular based studies to increase the heavy metal remediation ability of microbes, strategies to improve the metal resistance of microbes, methods to improve biosorption by modifications of biosorbents are expected to add more thrust in the advancements of biosorption in the near future (Qin et al., 2020).
4. Conclusion

Heavy metal distribution and associated pollution are quite vast, demanding timely action in certain instances. In such a scenario, to confine its remediation exclusively by one method would be unwise for effective and safe removal of heavy metals. Moreover, the drawbacks and limitations of one method of remediation can be overcome by combinatorial approaches. Thus a multidisciplinary approach using different physico-chemical-biological methods to address heavy metal pollution would be effective. Combinations of physical and biological methods pose less environmental toxicity and should be selected to improve heavy metal uptake. The choice of no energy consuming heavy metal remediation methods like adsorption using modified adsorbents to increase their specificity and efficiency. However, the use of energy utilising techniques such as vitrification cannot be avoided when handling the spread of radioactive heavy metals. Chemical methods are routinely used in waste water treatment with the aim of getting fast results, but attempts should be made to achieve remediation with the least expense of chemicals, simultaneously incorporating nanobased particle based metal recovery, biosorption and other adsorption strategies. The restoration of heavily polluted soil to self-sustainable fertile lands is possible by adopting methods of phytoremediation as well as the use of biostimulation and bioaugmentation of microbes in such environments. The use of such natural resources to remediate nature though not fast acting, yield long lasting eco-friendly solutions to combat heavy metal pollution.

Heavy metal pollution often occurs yielding a variety of metals rather than single type of members, necessitating the use of methods that can deal with the wide array of heavy metals. Thus the development of consortiums capable of remediating variety of heavy metals would be more promising. The use of microbial consortiums along with other methods would aid to reduce the heavy metal load to permissible limits and overcome the high concentration
induced microbial death and associated discrepancies in the realistic environment. Finally, the technological ease to recover heavy metals from the remediated agent for further use would be an added advantage to address both the problem of heavy metal pollution and heavy metal demand; thereby uplifting the principles of reduce, recycle, and reuse.

Acknowledgement

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### Table 1: Physical remediation methods for heavy metals

<table>
<thead>
<tr>
<th>Heavy metal</th>
<th>Type of physical remediation</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb, Cd</td>
<td>Soil replacement/ isolation</td>
<td>(Bodocsi et al., 1995; Douay et al., 2008)</td>
</tr>
<tr>
<td>Mn, Fe, Cu, Ni, Hg, Zn, Pb, Ag</td>
<td>Vitrification</td>
<td>(Dellisanti et al., 2009; Navarro et al., 2013)</td>
</tr>
<tr>
<td>As, Cu, Hg, Pb, Cd, Cs</td>
<td>Electrokinetic</td>
<td>(Iannelli et al., 2015; Lee et al., 2016; Mao et al., 2016; Rosestolato et al., 2015; Suzuki et al., 2014)</td>
</tr>
<tr>
<td>Ar</td>
<td>Particle-trapping system (PTS)</td>
<td>(Khoei et al., 2018)</td>
</tr>
</tbody>
</table>
Table 2: An outline of Microbes used in heavy metal removal

<table>
<thead>
<tr>
<th>Name of the microbe</th>
<th>Metabolite/Agent involved</th>
<th>Remediation in</th>
<th>Heavy metal remediated</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arbuscular fungi with <em>Robinia pseudoacacia</em> L.</td>
<td>Plants- fungal symbiont</td>
<td></td>
<td>Cd</td>
<td>(Wang et al., 2021b)</td>
</tr>
<tr>
<td><em>Aspergillus niger</em>, <em>Aspergillus foetidus</em> and <em>Penicillium simplicissimum</em></td>
<td>Fungal biomass</td>
<td></td>
<td>Ni, Co, Mo, V, Mn, Fe, W and Zn</td>
<td>(Anahid et al., 2011)</td>
</tr>
<tr>
<td><em>Trichoderma</em></td>
<td>Harzianic acid</td>
<td>Cd$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and Pb$^{2+}$</td>
<td>(Tommaso et al., 2021)</td>
<td></td>
</tr>
<tr>
<td>Cyanobacteria</td>
<td>exopolysaccharides</td>
<td>Cd, Ni, Zn, Pb</td>
<td>Cu$^{2+}$ and Zn$^{2+}$</td>
<td>(Yadav et al., 2021)</td>
</tr>
<tr>
<td><em>Pseudomonas putida</em></td>
<td>Dead cell mass in agar bead</td>
<td></td>
<td></td>
<td>(Meringer et al., 2021)</td>
</tr>
<tr>
<td><em>G. thermodenitrificans</em></td>
<td>dead biomass</td>
<td>Fe(+3)&gt;Cr(+3)&gt;Co(+2)&gt;Cu(+2)&gt;Zn(+2)&gt;Cd(+2)&gt;Ag(+)&gt;Pb(+2)</td>
<td></td>
<td>(Chatterjee et al., 2010)</td>
</tr>
<tr>
<td><em>Lysobacter</em>, <em>Kaistobacter</em> and <em>Pontibacter</em></td>
<td>Found in rhizosphere of <em>Trifolium repens</em> L</td>
<td></td>
<td>Cr$_2$O$_7^{2-}$, Cd$^{2+}$ and Pb$^{2+}$</td>
<td>(Lin et al., 2021)</td>
</tr>
</tbody>
</table>
### Table 3: List of Plants involved in heavy metal remediation

<table>
<thead>
<tr>
<th>Plant Involved</th>
<th>Heavy metal removed</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Trifolium repens</em> L.</td>
<td>Cr(_2)O(_7^{2-}), Cd(^{2+}) and Pb(^{2+})</td>
<td>(Lin et al., 2021)</td>
</tr>
<tr>
<td><em>Pinus sylvestris</em> L.</td>
<td>Zn, Cu, Mn, Ni, Pb</td>
<td>(Çomaklı and Bingöl, 2021)</td>
</tr>
<tr>
<td><em>Acorus calamus</em> L</td>
<td>Cr, Ni, Cu, Zn, and Cd</td>
<td>(Wang et al., 2021a)</td>
</tr>
<tr>
<td><em>Tagete serecta</em> L.</td>
<td>Zn and Cd</td>
<td>(Madanan et al., 2021)</td>
</tr>
<tr>
<td><em>Prospis laevigata</em></td>
<td>chromium (VI) and cadmium (II)</td>
<td>(Buendía-González et al., 2010)</td>
</tr>
<tr>
<td><em>Salsola kali</em></td>
<td>Cadmium</td>
<td>(de la Rosa et al., 2004)</td>
</tr>
<tr>
<td>Desert Marigold</td>
<td>Arsenic</td>
<td>(Harvey, 2021)</td>
</tr>
<tr>
<td><em>Crassula helmsii</em></td>
<td>Copper</td>
<td>(Corzo Remigio et al., 2021)</td>
</tr>
<tr>
<td><em>Noccaea brachypetala</em></td>
<td>Zn and Cd</td>
<td>(Martos et al., 2021)</td>
</tr>
<tr>
<td><em>Cyperus alternifolius</em></td>
<td>Pb, Zn, and Cd</td>
<td>(Yang et al., 2017)</td>
</tr>
</tbody>
</table>
### Table 4: List of wide range of algae for the treatment of heavy metals

<table>
<thead>
<tr>
<th>Name of the Algae</th>
<th>Heavy metal removal</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Sargassum carpophyllum (brown algae), Caulerpa lentillifera (green algae)</em></td>
<td>Pb²⁺, Cd²⁺, Cu²⁺, and Mn²⁺</td>
<td>(Li et al., 2020)</td>
</tr>
<tr>
<td><em>Chlorella kessleri (green algae)</em></td>
<td>Pb²⁺, Co²⁺, Cu²⁺, Cd²⁺, Cr²⁺</td>
<td>(Sultana et al., 2020)</td>
</tr>
<tr>
<td><strong>High selectivity for Cu</strong></td>
<td></td>
<td>(Son et al., 2018)</td>
</tr>
<tr>
<td>Kelp (Biochar of kelp magnetised)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Anabaena, Phormidium, Nostoc, Spirogyra, Navicula, Oscillatoria, Oedogonium, Hydrodictyon, Cymbella</em></td>
<td>Fe, Cu, Zn, Ni, Cr, Cd, and As</td>
<td>(Kumari, 2021)</td>
</tr>
<tr>
<td><em>Fucus vesiculosus</em></td>
<td>Pb(II), Cu(II), Cd(II), Zn(II) and Ni(II)</td>
<td>(Demey et al., 2018)</td>
</tr>
<tr>
<td><em>Caulerpa lentillifera (algae)</em></td>
<td>Dried macroalgae</td>
<td>(Apiratikul and Pavasant, 2008)</td>
</tr>
<tr>
<td><em>Ulva fasciata</em></td>
<td>Cd²⁺ and Zn²⁺</td>
<td>(Abdelhamid et al., 2021)</td>
</tr>
<tr>
<td>Name of remediation method</td>
<td>Advantage</td>
<td>Disadvantage</td>
</tr>
<tr>
<td>---------------------------</td>
<td>-----------</td>
<td>--------------</td>
</tr>
</tbody>
</table>
| Adsorption                | • Flexibility in design  
                           • Reversible  
                           • High quality of effluent  
                           • Simple  
                           • Cost effective adsorbents available  
                           • Applicable for low & high range contaminants  
                           • Can alter the selectivity of adsorbate by modifications | • Adsorption capacity varies on adsorbent  
                           • Cost of adsorbent varies  
                           • Adsorbent need to be regenerated |
| Soil replacement          | • treatment of heavily polluted small areas of soil  
                           • designed to prevent ground water infiltration of metals | • high cost as soil importing required  
                           • limitations in its applicability in agricultural land as fertility lost |
| Vitrification             | • Applicable in treatment and prevention spread of organics, inorganics and even radionucleotides to environment | • Cost effective only for small sites  
                           • Does not make soil suitable for cultivation  
                           • Success depends on conductivity and alkali content of the soil |
| Electrokinetic separation | • operates wells for solids having low permeability  
                           • Easy to install  
                           • Economically feasible | • Energy consuming  
                           • Fluctuation in soil pH is a limiting factor  
                           • High sludge generated when combined with other chemical coagulation techniques |
| Nanoremediation           | • selective removal of heavy metals  
                           • on-site, or in situ, treatment method  
                           • treatment of recalcitrant compounds | • concerns exist on nanoparticle prevalence in environment but can be overcome by combining |
<table>
<thead>
<tr>
<th>Chemical methods</th>
<th>Nanoparticles with magnetic particles aiding in its recovery from environment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>relatively more fast in action</td>
</tr>
<tr>
<td></td>
<td>highly efficient</td>
</tr>
<tr>
<td>Phytoremediation</td>
<td>Large amount of chemicals needed</td>
</tr>
<tr>
<td></td>
<td>easy operation</td>
</tr>
<tr>
<td></td>
<td>requiring no instrumentation</td>
</tr>
<tr>
<td></td>
<td>High sludge formation</td>
</tr>
<tr>
<td></td>
<td>simplicity</td>
</tr>
<tr>
<td></td>
<td>Inhibit inherent microbes</td>
</tr>
<tr>
<td>Phytoremediation</td>
<td>Concerns of entering food chain</td>
</tr>
<tr>
<td></td>
<td>simply relocates toxic heavy metals</td>
</tr>
<tr>
<td></td>
<td>it does not remove them from the locale</td>
</tr>
<tr>
<td>Microbes</td>
<td>applicable to concentrations not harmful to microbes</td>
</tr>
<tr>
<td></td>
<td>Cost effective</td>
</tr>
<tr>
<td></td>
<td>Eco-friendly</td>
</tr>
<tr>
<td></td>
<td>Restore the ecosystem</td>
</tr>
<tr>
<td></td>
<td>So at high concentrations might not be effective</td>
</tr>
<tr>
<td></td>
<td>High sludge formation</td>
</tr>
<tr>
<td></td>
<td>Inhibit inherent microbes</td>
</tr>
<tr>
<td></td>
<td>Availability of metal accumulators capable of growing in different niches</td>
</tr>
<tr>
<td></td>
<td>Optimization of process needed</td>
</tr>
<tr>
<td>Algae</td>
<td>Recovery of heavy metals needs post treatment</td>
</tr>
<tr>
<td></td>
<td>Efficient</td>
</tr>
<tr>
<td></td>
<td>Recovery of heavy metal possible</td>
</tr>
<tr>
<td></td>
<td>low chemical resistance,</td>
</tr>
<tr>
<td></td>
<td>low mechanical strength</td>
</tr>
<tr>
<td></td>
<td>optimization of process needed</td>
</tr>
</tbody>
</table>
Fig. 1. A depiction on the various principles of heavy metal Biosorption