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Introduction of heavy metals contamination in the water: A review on source, toxicity and remediation methods

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ABSTRACT

Different approaches that offer various benefits for the remediation of contaminated waters are being researched as the problem worsens. The global issue of heavy metal poisoning of water from industrial discharge is quite serious. As a result, both environmental and human health are negatively impacted. Various traditional technologies have been employed to treat water, but they can be costly and/or inefficient, particularly when treating industrial water. A technique called phycoremediation is used to successfully remove metal ions from river and sewer water. In aquatic habitats, microalgae are primarily responsible for naturally sequestering trace metals. They have high-affinity metal-binding groups on their cell surfaces, large surface volume ratios, and effective metal absorption and storage mechanisms, which all contribute to their capacity to adsorb and metabolise trace metals. In this context, algae offer an environmentally safe and sustainable alternative for eliminating heavy metals from polluted water. This review study covers the primary sources of heavy metals, their adverse effects on humans, the possibility of algae in the remediation of these heavy metals, and their absorption mechanism. Additionally, it provides a broad overview of the chances to improve efficacy, selectivity, and cost-effectiveness as well as their interactions with the extracellular polymeric molecules that stressed microalgae release into the extracellular environment.

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INTRODUCTION

Heavy metal contamination has garnered significant attention in recent years due to its potential to cause adverse biological effects in aquatic environments. Such effects can lead to structural changes in local planktonic communities, reducing biodiversity and disrupting the food chain and internal ecosystem balance (Pérez-Rama *et al.,* 2002). The term "heavy metal" refers to metals that exhibit toxicity. Nevertheless, the term is predominantly employed in informal contexts and lacks a formal definition from any authoritative body, such as IUPAC (Duffus, 2002). Heavy metals are defined in various ways based on specific physical, chemical, or biological properties, such as density (specific gravity), atomic weight and number, and other chemical characteristics. Some definitions lack a clear basis, relying instead on toxicity or non-chemical criteria (Duffus, 2002). Most definitions lack a connection to the toxicity of these metals for living organisms, as no correlation between density, atomic weight, or molecular weight and toxicity has been established (Duffus, 2002). Toxic metals refer to elements, not exclusively metals, frequently utilised in industrial applications, and are generally harmful to living organisms, even at low concentrations (Volesky and Naja, 2005). Examples include As, Cd, Cr, Cu, Pb, Hg, Ni, Se, and Zn (Scott and Smith, 1981). Selenium (Se) and arsenic (As) are often referred to as "heavy metals," even though these elements are not metallic in nature (Kabata-Pendias, 2000). When evaluating toxic properties, these elements are categorised within the same group as other toxic elements and are referred to as toxic metals (Kabata-Pendias, 2000).

The application of microbial biomass for the extraction of heavy metal cations from aqueous solutions has garnered significant attention due to its technical viability and economic suitability as an alternative to physicochemical methods, such as precipitation, ion exchange, and membrane processes. (Tien, 2002). Microalgae have been identified as possible biosorbents for heavy metal cations in wastewater due to their advantageous characteristics: low cost, immediate availability, relatively large specific surface area, and strong binding affinity (Tien, 2002; Gong *et al.,* 2005a). Furthermore, they utilise light as an energy source, enabling metabolism without the necessity of organic carbon sources, in contrast to the rigorous requirements of bacteria and fungi (Dönmez and Aksu, 2002). Furthermore, when juxtaposed with biological materials such as fungi, bacteria, and yeasts, microalgae exhibit superior heavy metal uptake capacity in certain instances (Tüzün *et al.,* 2005), primarily due to their cell walls, which are comprised of polysaccharides, proteins, and lipids. These components provide various functional groups, including carboxyl, hydroxyl, sulphate, phosphate, and amine moieties, all of which are recognised for their strong affinity for binding metal ions (Rangsayatorn *et al.,* 2002; Gong *et al.,* 2005a; Kaduková and Virčíková, 2005). Consequently, both viable and non-viable algal cells have been progressively utilised as biosorbents, particularly to support extensive bioremediation initiatives (Tam *et al.,* 1998; Al-Rub *et al.,* 2004; Han *et al.,* 2006; Deng *et al.,* 2007). Nonetheless, non-living cells offer greater benefits for industrial applications, as they remain unaffected by metal ion toxicity and unfavourable operating conditions (Chu and Hashim, 2004); additionally, substantial quantities are easily and cost-effectively obtainable as by-products of biotechnology industries (Cruz *et al.,* 2004).

Phycoremediation is a greener and more cost-effective method for removing heavy metals from wastewater. It involves using algae-based biosorbents to remove nutrients and xenobiotics, treating wastewater contaminated with acid and heavy metals, sequestering CO_2, and detecting toxic compounds. Algae can absorb various pollutants, including pesticides and heavy metals.

The high heavy metal ion uptake capacity and cost-effective cultivation of algal biomass make it highly effective for wastewater bioremediation. This review provides an overview of heavy metals as potential contaminants in aquatic ecosystems and the phycoremediation potential of algae.

Heavy metals as potential contaminants of the aquatic ecosystem

Water may be contaminated by several geographical processes, like the breaking down of rocks, volcanic eruptions, and the entrance of these particles into aquatic systems, including rivers and seas (Bagul *et al.,* 2015). Mercury mostly comes from natural water bodies of water degassing from the crust of the Earth released from volcanoes. Many human activities, like mining operations, extraction, and smelting of several metals, can release heavy metals. The industrial sector takes metals from natural sources and then sends them to the atmosphere. The several anthropogenic routes by which heavy metals might find their way into the environment are smelting or treating of ores of metal, mining operations, burning of coal, petrol, and kerosene oil, the release of agricultural, household, and industrial waste, and vehicle exhausts (Hange and Awofolu, 2017). Among the heavy metals, Cd, Pb, As, Se, Hg, Mn, Zn, etc., some are poisonous and create environmental problems. Urban, industrial, and household wastes include toxic compounds such as heavy metals that endanger plants, animals, people, and every ecosystem (Fig. 1).

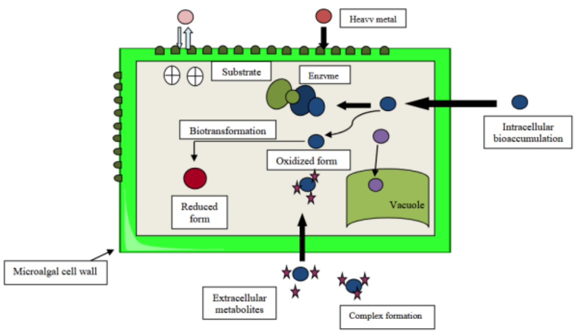

Fig. 1. Bioaccumulation of heavy metals by an algal cell

Considered to be the most crucial elements for raising the amounts of these trace metals, mostly heavy metals, through water run-off are industry development and increased urbanisation (Singh and Kalamdhad, 2011). These sources discharge several hazardous toxins that find their way into the environment, settle as sediments or in soil, and through the water run-off, find their way into aquatic ecosystems, and have negative effects on water bodies (Abida Begum *et al.,* 2009). Of the roughly 50 elements that are regarded as heavy metals, 17 are the most harmful ones (Ali and Khan, 2017).

Toxicity of heavy metals

Historically, it was thought that metal ions played a minimal role in animal and plant systems, with the living world primarily associated with organic chemistry. The biological significance of metal ions is now well established; life cannot exist without metal ions, indicating that life encompasses both inorganic and organic components (Förstner, 1981). Some heavy metals, classified as 'essential' (e.g., copper, molybdenum, zinc), are recognised for their roles in metabolic reactions. In contrast, the metabolic or physiological requirements of 'non-essential' heavy metals, such as cadmium, lead, and mercury, remain unclear. High concentrations of heavy metals are toxic to algae, although the degree of toxicity varies between metals classified as 'essential' and those deemed 'non-essential.' Without essential heavy metals, algae exhibit impaired growth, leading to disruptions in physiological and biochemical processes, or the abandonment of critical aspects of their life cycle or metabolism. While growth proceeds normally at lower concentrations of essential heavy metals, elevated concentrations typically result in toxicity or lethality. The effects of certain significant (both essential and non-essential) heavy metals on algae are outlined in the subsequent paragraphs (Rai *et al.,* 1981) (Table 1).

Arsenic

Arsenic (As) is a toxic heavy metal that contaminates drinkable water in various countries, including Argentina, Bangladesh, Chile, China, Finland, India, Southeast Asia, and the United States. It is classified as a class A and category 1 carcinogen by the USEPA (Wang *et al.,* 2014; Upadhyay *et al.,* 2016; Arora *et al.,* 2018a). Anthropogenic activities like burning fossil fuels, mining, fertilisers, pesticides, smelting, electrolysis, and sewage sludge contribute to widespread arsenic pollution (Singh *et al.,* 2016; Arora *et al.,* 2017). As can cause lung, skin, kidney, and bladder cancers at low concentrations, while higher concentrations can cause arsenicosis, arsenical dermatitis, cardiovascular disease, diabetes, and other health issues (Li *et al.,* 2019). It also damages DNA and cell organelles in plants and microalgae, causing lipid peroxidation and protein degradation (Upadhyay *et al.,* 2016).

Mercury

Mercury, a naturally occurring metal, is a significant environmental hazard due to its impact on the environment, including its presence in water bodies. It reduces chlorophyll levels, slows algae growth, inhibits photosynthesis, and lowers nitrogen levels (Stratton *et al.,* 1979; Rai *et al.,* 1981). When added to algal growth media, mercury increases the carotenoid: chlorophyll ratio and increases RNA, DNA, and protein in *Chlorella* sp. (De Filippis and Pallaghy, 1976; Rai *et al.,* 1981). However, exposure to phenylmercuric acetate decreases these amounts. Mercury also causes a significant loss of potassium ions and enhances cell permeability, leading to potassium efflux (Barber and Shieh, 1972). Mercury exposure occurs when people breathe in elemental mercury vapours or consume contaminated fish and shellfish. Mercury cannot be eliminated by cooking, leading to toxicity or Minamata disorders. Mercury can come into contact with people through various means, such as manufacturing or the consumption of contaminated fish and shellfish.

Table 1. Adverse effects of heavy metals

Metals	Adverse effects	References
As	Carcinogenic effects, Hyperpigmentation, melanosis, and keratosis in humans, genotoxic, as it leads to the generation of ROS and causes lipid peroxidation. Immunotoxic, modulates co-receptor expression, causes black foot disease	(Yedjou and Tchounwou, 2006; Sutton and Tchounwou, 2007)
Hg	Mutagenic effects, Minamata disease, Hampers cholesterol	(Tchounwou *et al.,* 2004; Gautam *et al.,* 2014)
Cd	This leads to severe bone and kidney damage in humans, anaemia, bronchitis, emphysema, and Acute toxic effects in children.	(Singh and Singh, 2017; Chowdhary *et al.,* 2018; Khan *et al.,* 2018)
Zn	Causes anaemia, Phytotoxic, leads to a decrease in muscular coordination, Causes pain in the abdomen.	(Asati *et al.,* 2016)
Cu	Phytotoxic, damages a range of aquatic fauna, causes Corrosion and mucosal irritation, disturbs the central nervous system, and can lead to depression.	(Sutton and Tchounwou , 2007)
Cr	Irritates the gastrointestinal mucosa, Nephritis, and death in humans at higher doses of Cr (VI)	(Shukla *et al.,* 2018)
Ni	High concentration may lead to DNA damage, a Negative effect on fauna, and cause phytotoxicity.	(Sutton and Tchounwou , 2007)
Pb	Phytotoxic, High concentration may lead to metabolic poisoning, Toxic to humans, aquatic fauna, and livestock, Hypertension leading to brain damage, may lead to fatigue, irritability, anaemia, and behavioural changes in children.	(Tchounwou *et al.,* 2004; Fatima *et al.,* 2019; Obasi and Akudinobi, 2020)

Cadmium

Mining operations in the foothills of the Himalayas are responsible for cadmium poisoning in rivers, worsening kidney failure, and bone weakness linked to itai-itai sickness. Heavy metal cadmium poses a significant risk to human health and the ecosystem. It is widely dispersed and has a middling concentration. Studies have shown cell lysis, filament elongation, and loss of cellular contents in blue-green algae, *Anabaena inaequalis* (Stratton and Corke, 1979). Cadmium damage is evident in the fine structure of freshwater algae, with dense intramitochondrial granules (Silverberg, 1976). Cadmium is used in various industrial processes, including batteries, pigments, and metals. Environmental concerns have led to reduced commercial usage, despite the increased use of batteries.

Lead

Lead can enter drinking water due to deteriorating plumbing systems in areas with high acidity or low mineral content, corroding pipes and fixtures. Lead toxicity targets the nervous system, with adults being more severely affected in the peripheral nervous system and children more severely affected in the central nervous system. (Cory-Slechta, 1996; Bellinger, 2004; Brent, 2006). Lead also affects the haematological system by blocking enzymes necessary for haemoglobin production and shortening the lifespan of erythrocytes. This results in anaemia, with two types: frank anaemia and hemolytic anaemia (Cornelis *et al.,* 2005; Guidotti *et al.,* 2008). Lead is absorbed by mitochondria, leading to enlargement and deformation of cristae, dissociated energy metabolism, blocked respiration, and altered calcium kinetics (Holtzman *et al.,* 1984). Lead has a binary effect on neurotransmitter release, increasing spontaneous release and decreasing induced release (Bressler and Goldstein, 1991).

Mechanisms of heavy metal uptake in algae

Algae, with their high rate of photosynthesis and increased oxygen emissions, promote the aerobic breakdown of organic molecules. They use biochemical and enzymatic processes to reduce pollution and use waste as food. Algal metabolic pathways can volatilize, purify, and alter heavy metal and xenobiotic pollution. Microalgae, through phycoremediation, can remove and degrade environmental toxicants like heavy metals and organic pollutants. They have evolved defence mechanisms to withstand pollutants and detoxify harmful substances. Heavy metal removal occurs through various processes, including metabolism and passive adsorption (Fig. 2).

Biosorption

Biosorption is a quick, reversible process that occurs independently of cellular metabolism, involving ions binding to functional groups on biomass surfaces. (Davis *et al.,* 2003). It is a simple and effective method for extracting metals from diluted solutions, requiring little capital commitment and using low-cost, renewable sorbents from secondary sources and cultures, including fungi, algae, bacteria, and aquaculture and agro-industrial wastes. (Davis *et al.,* 2003; Beni and Esmaeili, 2020). The internal compartment and the exterior environment are connected by the cell wall, which is made up of macromolecules such as lipids, proteins, and carbohydrates (Macfie and Welbourn, 2000).

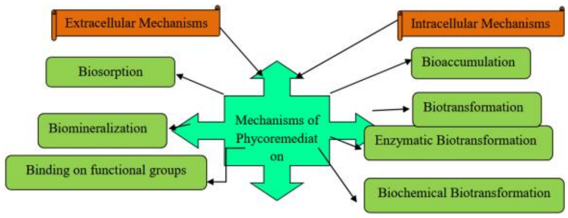

Fig. 2. Mechanism of phycoremediation

According to Javanbakht *et al.* (2014), it has negatively charged functional groups on its surface, including sulfhydryl, carboxyl, amino, hydroxyl, phosphate, phenol, and sulfate elements. These negatively charged groups are responsible for the removal of heavy metals (HMs) by the outer layer of the cell wall (Saavedra *et al.,* 2018; Leong and Chang, 2020; Singh *et al.,* 2021). The composition, structure, and characteristics of the cell wall are essential for the investigation of biosorption mechanisms (Podder and Majumder, 2017). Algae reduce metal damage through metal exclusion and excretion, as well as the synthesis of proteins and binding molecules like glutathione (GSH) and metallothioneins (MTs) (Wang *et al.,* 2016; Salama *et al.,* 2019).

Toxic metals and other detrimental substances often pose an imminent threat to microalgae in aquatic environments. These species have evolved the adaptive process of EPS production as a defensive strategy. Typically, tissue stimulation results in an elevation of EPS production. The Chlorophyta phylum contains microalgae strains commonly used in phytocoremediation, particularly those from the genera *Chlorella* and *Scenedesmus* (Spain *et al.,* 2021). Yu *et al.* (2019) indicated that the extracellular polymeric substances (EPS) of *Chlamydomonas reinhardtii* significantly increased with exposure to cadmium. Li *et al.* (2021) demonstrated that *C. reinhardtii* produces elevated levels of EPS when exposed to Pb(II) and Cd(II) stressors.

Furthermore, Zhang *et al.* (2015) found that Cu absorption is caused by EPS and not intracellular chelation, as evidenced by the increased EPS yields in Cu-enriched *Chlorella* sp. cultures.

Comparing *C. pyrenoidosa* cells treated with and untreated with EPS shows that EPS increases tolerance to As ions, decreases intracellular accumulation, and improves adsorption capability (Zhang *et al.,* 2020). It appears that EPS can establish an extracellular protective barrier on the cell wall's surface, thereby protecting the intracellular environment from the harmful effects of heavy metals. Consequently, their excretion facilitates the maintenance of cellular integrity as a survival strategy (Hou *et al.,* 2017; Naveed *et al.,* 2019). Moreover, EPS comprises several charged hydrophobic groups that are adept at actively binding to heavy metals (Zhang *et al.,* 2020). The primary functional groups implicated in the biosorption of heavy metals are present in some algal cell wall constituents, such as fucoidan and alginate (Anastopoulos and Kyzas, 2015; Zeraatkar *et al.,* 2016). Electrostatic and van der Waals forces contribute to the physical interaction between metals and biosorbents, while complexation, ion exchange, proton shift, and metal chelation pertain to the chemical interactions involved (Crist *et al.,* 1999). Heavy metal ions from wastewater integrate with small ions like Na^{+}, Ca^{2+}, and K^{+} that are on the outer layer of algae. Key factors, such as metal selection and regeneration ability, must be met for this process to be possible. Changing the algal material chemically, such as by cross-linking it with epichlorohydrin or oxidising it with potassium permanganate, makes biosorption more selective (Luo *et al.,* 2006).

Bioaccumulation

Bioaccumulation is a metabolic process affected by several causes, unlike biosorption. The term refers to the accumulation of heavy metals in the cell membranes of live microalgae via passive and/or active transport pathways (Chojnacka, 2010). The process consists of two successive phases: the initial phase entails the fast, passive, and non-specific absorption of metal ions onto the cell wall. Subsequently, active or passive transport occurs across the cell wall and plasma membrane into the cytoplasm (Kumar *et al.,* 2015). Algae employ both extracellular and intracellular metal binding strategies, such as complexation, physical adsorption, ion exchange, and chelation, to mitigate the toxicity associated with heavy metals (Mantzorou *et al.,* 2018).

These methods effectively convert harmful metals into less harmful or non-hazardous forms (Mustapha and Halimoon, 2015; Mantzorou *et al.,* 2018). Algae detoxify metals via several mechanisms, such as binding to specific intracellular organelles, transporting metals to cellular components like polyphosphate vacuoles, utilising efflux pumps to expel metals into solution, and synthesising class III metallothioneins or phytochelatins (Perales-Vela *et al.,* 2006; Tripathi and Poluri, 2021).

Phytochelatins are small peptides, ranging in molecular weight from 2 to 10 kDa, that exhibit metal-binding properties. Torres *et al.* (2008) states that phytochelatin synthase is a constitutive enzyme responsible for the synthesis of phytochelatins. The synthesis of these compounds from γ-glutamylcysteine, hydroxymethyl-glutathione, homo-glutathione, and orglutathione is mediated by phytochelatin synthase, a transpeptidase that necessitates heavy metals for its post-translational activation. Most algae and all higher plants can synthesise phytochelatins (Ahner *et al.,* 1995). Kinetic experiments conducted by Cobbett and Goldsbrough (2002) demonstrate that phytochelatin production occurs rapidly, within several minutes, and is independent of de novo protein synthesis. Phytochelatin synthase can be activated in both in vivo and in vitro conditions by various metalloids and metals, such as As, Cu, Cd, Pb, Ag, Sn, Hg, Zn, and Au (Bačkor *et al.,* 2007). Cadmium (Cd) has been identified as a potential activator of phytochelatin synthesis, facilitating the production of phytochelatins with more stable chains, specifically up to PC5 (Chmielewska and Medved, 2001; Bačkor *et al.,* 2007). Heavy metals exhibit reduced toxicity to living algae when they precipitate in the presence of sulphide, phosphate, or carbonate.

Cladophora glomerata, a species of green algae, demonstrated the capacity to extract the following heavy metals from a refinery sewage lagoon: Pb at 7.9 mg kg^{-1}, Cd at 0.1 mg kg^{-1}, Ni at 15.6 mg kg^{-1}, Cr at 1.7 mg kg^{-1}, and V at 37.7 mg kg^{-1} (Salama *et al.,* 2019). The brown macroalga *Fucus vesiculosus* demonstrates significant efficacy in the removal of heavy metals (HMs) from contaminated saltwater, achieving reductions of 65%, 95%, and 76% for lead, mercury, and copper, respectively. (Henriques *et al.,* 2017).

Biotransformation

Biotransformation denotes the metabolic process by which endogenous or exogenous substances are converted into molecules that differ in toxicity (detoxification vs toxication), excretability (hydrophobic versus hydrophilic), and activity (activation versus deactivation) (Rourke and Sinal, 2014). Biotransformation in algae primarily involves the enzymatic and biochemical transformation of heavy metals, although it has also been employed for detoxification processes. Heavy metals are non-degradable; thus, enzymatic biotransformation converts them into less toxic inorganic complexes. (Pradhan *et al.,* 2022). Biotransformation entails the reduction of valuable heavy metals through electron transfer, subsequently converting them into organic heavy metal compounds (Yen *et al.,* 2017).

Enzymatic biotransformation

Enzymatic biotransformation of heavy metals involves the chemical conversion of a highly toxic form into a less toxic variant through oxidation-reduction reactions. Heavy metals (HMs) are non-biodegradable; however, their harmful effects can be alleviated by transforming their oxidation states into inorganic complexes. The role of oxidoreductase enzymes in the detoxification of heavy metals by microalgae has been largely neglected in research. Leong and Chang (2020) identify chromate reductases, mercuric reductase, and arsenate reductase as the primary redox enzymes in microalgae. Studies by Lee *et al.* (2017) and Yen *et al.* (2017) demonstrate that *C. vulgaris* strains can convert Cr(VI) to Cr(III) via an enzymatic reaction facilitated by chromate reductase. Kelly *et al.* (2006) revealed that the microalgae strains *C. fusca*, *Galdieria sulphuraria*, and *Selenastrum minutum* can facilitate the biotransformation of Hg^{2+} into elemental Hg^0 and metacinnabar (β-HgS) by mercuric reductase. *C. reinhardtii*, a green microalga, has been identified as possessing arsenate reductase (Yin *et al.,* 2011).

Biochemical transformations of HMs

Microalgal cells can employ biochemical processes to mitigate heavy metals during phycoremediation. The transfer of electrons to the reduced form of GSH facilitates the reduction of chromium from the hexavalent to the trivalent oxidation state (Yen *et al.,* 2017). Additionally, multiple detoxifying pathways can mitigate the toxicity of inorganic arsenic. Several microalgae species have demonstrated the ability to reduce As(V) to As(III). Karadjova *et al.* (2008) demonstrated that following 72 hours of exposure to As(V), *C. salina* converted 32% of its total intracellular As(V) concentration to As(III). Hasegawa *et al.* (2001) Indicate that *C. aciculare* initially transformed the starting concentration of As(V) in the medium to As(III), which subsequently reached its peak during the exponential growth phase. As-species are commonly located in various cellular fractions of microalgae cells, including the lipid, cytosolic, cell membrane, and debris fractions. The detoxification process initiates with the reduction of As(V) to As(III), which is then methylated to monomethylarsonate (MMA(V)) through the action of oxidase and S-adenosylmethionine. After its conversion to DMA(III), the produced MMA is converted into various organoarsenicals, such as arsenolipids, arsenosugars, arsenobetaine, and arsenoribosides (Wang *et al.* 2015; Arora *et al.,* 2018).

Other biotransformation mechanisms of HMs

Alongside the previously documented intracellular heavy metal biotransformation process, the production of metal nanoparticles can occur both intracellularly and extracellularly, contingent upon the site of nanoparticle biosynthesis and the reductive agents involved (Hamida *et al.,* 2020). Microalgae can convert toxic heavy metals into less harmful forms by integrating them with proteins, lipids, carbohydrates, pigments, and other antioxidant compounds, effectively neutralising the metal ions' charge (Chaudhary *et al.,* 2020). Furthermore, in the extracellular environment, EPS, binding sites, organic ligands, and charged functional groups on cell surfaces may contribute to changes in the speciation of harmful heavy metals via redox processes (Naveed *et al.,* 2019). Priyadarshini *et al.* (2019) demonstrated that the intracellular environment, which contains polysaccharides, proteins, and pigments that act as reducing agents for stabilising metal ions and nanoparticles, is more complex than the extracellular biosynthesis of metal nanoparticles, which is comparatively simpler. *E. gracilis* can utilise both biological and non-biological volatilisation of mercury as a biotransformation method to mitigate the detrimental effects of mercury (Devars *et al.,* 2000). Deng *et al.* (2006b) demonstrated that a photoreduction pathway governed the Cr (VI) biotransformation in *C. vulgaris*.

Factors affecting heavy metal absorption

The biosorption efficacy was consistent within a temperature range of 20-35°C. (Ahalya *et al.,* 2003). Biosorbents, which are predominantly naturally occurring ion-exchanging organisms, possess weakly basic and acidic groups within their cell walls. Lowering the pH of metal solutions from 6.0 to 2.5 significantly decreases heavy metal uptake by various biomass types. The carboxyl groups present in algal and fungal cell walls demonstrate a moderate acidity (pKa between 3.5 and 5.5), which suggests pH-dependent metal absorption characteristics. The pH dependency of ion exchange between protons and metals on amino groups is reportedly analogous to that of carboxyl groups. An increase in biosorbent concentration affects binding sites, resulting in higher specific metal absorption at lower biosorbent concentrations (Gourdon *et al.,* 1990). Biosorption is employed in the treatment of multi-metal systems containing various metallic ions; thus, the removal of a specific metal ion is affected by the presence of other metal species (Deng and Wang, 2012). The presence of uranium, lead, mercury, and copper inhibits cobalt uptake by various microorganisms (Ahalya *et al.,* 2003; Gong *et al.,* 2005). Pretreating biomass with alkalies, acids, detergents, and heat enhances its metal affinity to the biosorbent (Ahalya *et al.,* 2003).

Algae as a tool for bioremediation

Seaweed is extensively employed in biosorption processes for wastewater treatment, effectively removing or decreasing hazardous heavy metal concentrations (He and Chen, 2014). The removal of heavy metals from aquatic environments is a pressing environmental issue, given the detrimental effects these elements have on living organisms (Adamu *et al.,* 2015). Some heavy metals are rapidly taken up by organisms, persist in the environment without breaking down, and can pose significant health risks, including carcinogenic effects, even at minimal concentrations. According to Arumugam *et al.* (2018), the main contributors to the accumulation of heavy metals in soils and groundwater are activities such as mining, smelting, the paint industry, the use of fertilisers, leather tanning, electroplating, alloy production, and battery manufacturing.

Cadmium is the metal most frequently studied for biosorption with algae; approximately 23% of publications address its environmental toxicity and the significance of its removal. Furthermore, this serves as a sign that biotechnology methods provide a viable alternative to traditional techniques. Subsequently, significant concentrations of heavy metals, extensively released through mining and industrial activities, are identified, notably copper (20%) and lead (19%). The biosorption of more prevalent metals, such as iron (3%), has been the subject of limited investigation due to the cost-effective and practicable process of precipitation through neutralising agents. Consequently, there is a lack of motivation for further exploration.

Brown seaweeds

Among the most hazardous heavy metals globally are chromium, nickel, copper, arsenic, cadmium, mercury, and lead (Islam *et al.,* 2015). Lead and chromium are among the most prevalent harmful cations found in wastewater. In a study conducted by Ali *et al.* (2020) regarding the biosorption of Pb and Cr in two species of brown seaweed, *Hydroclathrus clathratus* and *Cystoseira barbata*, it was found that there exists an inverse relationship between the concentration of the metal and its uptake. The optimal biosorption efficiency was achieved at 120 minutes, with a pH of 5 and an algae concentration of 10 g/L. The maximum uptakes for Pb and Cr biosorption are recorded at 4.97 and 7.19 mg/g for *H. clathratus*, and 4.61 and 7.30 mg/g for *C. barbata*, respectively. A study by Plaza Cazón *et al.* (2011) employed *Macrocystis pyrifera* for the extraction of zinc and cadmium from both mono- and bimetallic solutions. The findings indicated that the organism exhibited strong uptake capacities in both scenarios, aligning with previous research conducted on other species as documented in earlier studies (Mata *et al.,* 2008). *M. pyrifera* and *Undaria pinnatifida* effectively removed mercury and chromium from aqueous solutions. Research suggests that carboxylic and amino groups are crucial for chromium binding, while amino and sulfhydryl groups are linked to mercury assimilation. This suggests that the interactions are specific to the metals and their respective functional groups (Plaza *et al.,* 2011). The brown alga *Sargassum* sp. was utilised to extract Pb and Cu from stormwater, demonstrating biosorption capacities of 196.1 mg/g for Pb and 84.0 mg/g for Cu. Barquilha *et al.* (2019) utilised alginate derived from *Sargassum* sp. as a biosorbent to extract Ni and Cu ions from both actual electroplating effluents and synthetic solutions. The maximum sorption capacity (qmax) for Ni ions reaches 1.147 mmol/g, whereas Cu ions exhibit a qmax of 1.640 mmol/g. Torres (2020) indicates that biosorption has proven to be an effective method for eliminating it in this context. Sea farms are regarded as a dependable resource due to the diverse array of phytoplankton that can be cultivated. Yadav *et al.* ((2019) investigated the application of marine algae, specifically brown algae, for the removal of heavy metals from fluids via the processes of biosorption and bioaccumulation. The biomass of *Lessonia nigrescens* was employed to biosorb Cu from the solution at a pH of 5 over a contact period of 120 minutes. The Langmuir isotherm model demonstrated the most accurate data fit, resulting in a maximum biosorption capacity of 60.4 mg/g. Cu ions are captured in solution by the dead biomass of the brown algae *L. nigrescens* through surface interactions with various functional groups, such as amide, carboxyl, hydroxyl, and sulfonate groups, while amine groups do not play a role in this process (Cid *et al.,* 2018).

Red seaweeds

Ceramium virgatum, a red alga, was employed for cadmium extraction from aqueous solutions. The study examined the influence of temperature, pH, contact time, biomass dosage, and other experimental variables on the biosorption process. Sarı and Tuzen (2008) indicated that the biosorption capacity of *C. virgatum* monolayer for Cd(II) ions was measured at 39.7 mg/g. The bioadsorption of pretreated red algae *Gracilaria fisheri* for cadmium and copper was examined by Chaisuksan (2003). The maximum uptake levels recorded were 0.63 and 0.72 mmol/g, respectively. The absorption of cadmium and copper occurred rapidly, with 90% of the biosorption completed within a 30-minute timeframe. Alternatively, investigations have employed alginate extracted from the biomass of the marine red algae *Callithamnion corymbosum* to eliminate Cu(II), Co(II), and Zn(II) ions from aqueous solutions. The maximal biosorption capabilities are as follows: Cu(II) (64.52 mg/g) > Zn(II) (37.04 mg/g) > Co(II) (18.79 mg/g). The ideal conditions for biosorption were determined to be at a pH of 4.4, a biosorbent concentration of 2.0 g/L, and room temperature (Lucaci *et al.,* 2020). *Porphyra leucosticta* demonstrates efficiencies ranging from 70% to 75% for cadmium (Cd) and 90% to 95% for lead (Pb) following a mere two hours of exposure (Akbar and Hasan, 2024).

Green seaweeds

Da Costa and De França (2003) examined the accumulation of Cd ions by the microalga *Tetraselmis chuii*, focusing on both growing and dead cells. The green algae *Codium vermilara* were employed to extract copper with an efficiency of around 85%. This was achieved at a copper concentration of 48.8 mg/L, using an algae dose of 0.75 g/L, at a pH of 5.3, and during a contact period of 70.5 minutes (Fawzy, 2020). *Chlorella vulgaris* demonstrated a biosorption capacity for copper, achieving a recovery rate of 90.3% at a pH of 7, with a contact time of 105 minutes and an initial concentration of 20 mg/L (Indhumathi *et al.,* 2018). Research indicates that amine and carboxyl groups are the favoured chemical components present in green cell walls. The biosorption occurred extracellularly, as evidenced by the presence of copper on the cell surface. *Caulerpa racemosa* has been examined for its capacity to absorb cadmium (Cd) and hexavalent chromium (Cr VI), demonstrating a notable removal efficiency of 85%. In a separate study, *Caulerpa racemosa* demonstrated a moderate uptake of trivalent chromium (Cr III) and lead (Pb), achieving an efficiency of 50% (Raza'i *et al.,* 2022). The observed differences in performance among various metal ions indicate that *Caulerpa racemosa* could demonstrate a preference for specific metals, showing a stronger affinity for particular types. This characteristic underscores the necessity for additional investigation into the molecular mechanisms that regulate metal uptake and the formulation of refined remediation strategies customised for particular contaminants. Green macroalgae, including *Cladophora fascicularis*, have shown encouraging outcomes in the absorption of heavy metals. This species demonstrated the ability to eliminate lead (Pb) and copper (Cu) with a biosorption capacity of 1.61 mmol/g for Cu^{2+} and 0.96 mmol/g for Pb^{2+}. The data indicate that *Cladophora fascicularis* could be especially effective in addressing water pollution caused by copper and lead, which are prevalent contaminants in industrial wastewater (Deng *et al.,* 2006).

Blue-green algae

Cyanobacteria have certain qualities that make them a great choice for the removal of heavy metals. Such as EPS release, various transport mechanisms, and cell wall characteristics (Al-Amin *et al.,* 2021). It has been reported that several cyanobacterial species can sequester heavy metal ions through either biosorption or bioaccumulation, and frequently both. *Anabaena doliolum* (Goswami *et al.,* 2015), *Tolypothrix ceytonica* (Goswami *et al.,* 2015), *Cyanospira capsulata* and *Nostoc* PCC7936 (De Philippis *et al.,* 2003), *Gloeothece magna* (Mohamed, 2001), *Limnococcus* sp. (Sen *et al.,* 2018), *Microcystis* sp. (Rai and Tripathi, 2007), *Nostoc muscorum* (Roy *et al.,* 2015) are a few species that biosorb heavy metal ions through EPS. While some cyanobacterial species have been shown to bioaccumulate heavy metals within cells, *Synechococcus* sp. PCC 7942 (Rahman *et al.,* 2011), *Nostoc muscorum* (Rahman *et al.,* 2011), *Spirulina fusiformis* (Pandi *et al.,* 2009), and *Limnococcus* sp. (Sen *et al.,* 2018). Furthermore, several species, such as *Synechococcus* sp. PCC 7942, *Nostoc muscorum*, and *Limnococcus* sp. sequester the metal from water by both methods (Rahman *et al.,* 2011).

CONCLUSION

Heavy metal contamination of aquatic systems presents a significant challenge as it adversely affects both human health and various biological ecosystems. Various algal species have been identified as effective alternatives for removing or detoxifying heavy metals, providing promising options beyond traditional physicochemical remediation methods. The mechanisms of bioaccumulation and biosorption serve as effective methods for the removal of heavy metals from the environment. Algae-based phycoremediation offers a highly promising approach for addressing heavy metal pollution in aquatic ecosystems. A multitude of studies illustrate the effectiveness of algae species in extracting a range of toxic metals, such as lead (Pb), cadmium (Cd), chromium (Cr), and mercury (Hg), from polluted aquatic environments. While these results are encouraging, there are still obstacles to overcome, especially in expanding microalgae-based phycoremediation for large-scale industrial use. The differences in metal uptake rates among various species and under different environmental conditions, including pH and temperature, pose challenges for the standardisation of this process for broader application. Furthermore, the proper disposal or repurposing of metal-laden biomass presents a significant challenge, necessitating additional investigation to create affordable and eco-friendly solutions. Microalgae present a sustainable and economical solution for the removal of heavy metals, showcasing effectiveness across multiple species and types of metals. To maximise the potential of this technology, subsequent investigations should concentrate on refining growth conditions, creating effective disposal strategies, and enhancing the scalability of algae-based remediation systems. With ongoing investment, this environmentally friendly technology has the potential to significantly contribute to the purification of polluted water bodies and the rejuvenation of aquatic ecosystems.

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