

# Phycoremediation: Use of Algae to Sequester Heavy Metals

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**Abstract:** Industrialization, natural processes, and urbanization have potentially accelerated the pace and the level of heavy metals (HMs) in soil and underground water. These HMs may be accumulated in plants and animals when they take up such contaminated water, and then make their way into human food chains. Several remediation technologies have been employed to take up HMs. Diverse conventional means such as ion exchange, electrolytic technologies, and chemical extraction have been employed in the past, but the majority of these techniques are not economical for extensive projects and they need stringent control and continuous monitoring. These technologies also have low efficiency for effective removal of HMs. In this context, algae offer an eco-friendly and sustainable alternative for remediation of HMs from polluted water. The accumulation of HMs by macro and microalgae is advantageous for phycoremediation compared to other approaches that are not economical and not environmentally friendly. So, there is an urgent necessity to refine the chances of accumulation of HMs in algae, employing the techniques of genetic engineering to create transgenic species for over-expressing metallothioneins and phytochelatins, which may form complexes with HMs and store them in vacuoles to make the maximum use of phytoaccumulation while also removing hazardous metals from the aquatic habitats. This review outlines the major sources of HMs, their adverse effects on humans, the potential of algae in phytoremediation (called phycoremediation), and their uptake mechanism of HMs.

**Keywords:** heavy metals; phycoremediation; algae; aquatic ecosystem



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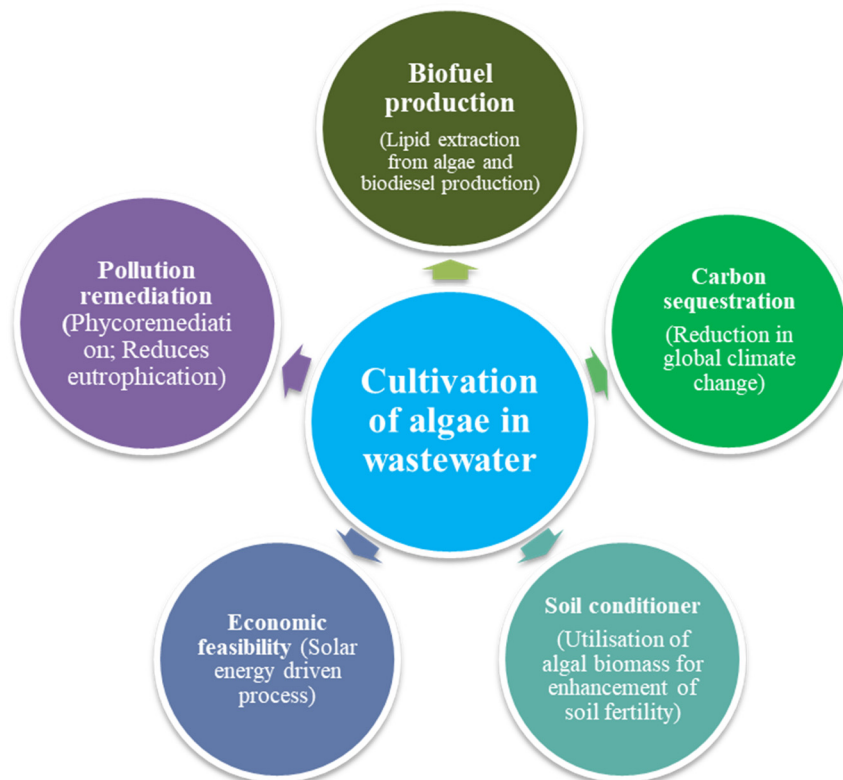
## 1. Introduction

Above and below groundwater contamination by HMs is a cause of grave concern [1]. Natural processes (e.g., floods, wind, and volcanic eruption) and anthropogenic activities (e.g., industrial effluents) are some of the ways that HMs are released into the environment [2–7]. Precipitation causes HMs in soil and air to become mixed in water bodies [8]. HMs are persistent and non-biodegradable in nature; they jeopardize human health and have negative effects on ecosystems [9–11]. Excess HMs in freshwater render it unfit for its designated purpose [12,13]. Hence, strict measures must be taken to reduce the level of HMs in wastewater below permitted limits prior to their discharge into natural reservoirs of water.

HMs are toxic to plants, animals, and overall ecosystem health [14,15]. HMs are accumulated in plants particularly through their roots [14] and enter the food chain. Increased lead (Pb) concentration in soils can decrease productivity, resulting in plants developing dark green leaves, decreased foliage, drooping of aged leaves, and dwarf brown roots [16–19]. Excess uptake of chromium (Cr), cadmium (Cd), lead (Pb), and manganese (Mn) can result in elevated rates of transpiration [20]. HMs elevate the amount of reactive oxygen species (ROS) that may harm fish and other aquatic life [21,22]. Humans are exposed to HMs mostly through accumulation of these metals at high concentrations, such as through ingestion of foods grown in such polluted soil [14].

Leaching, hydrolysis, polymer micro-encapsulation, chemical extraction, precipitation, ion exchange, and electrolytic technologies are a few conventional techniques used for the removal of HMs from polluted sites [23,24]. A major drawback is that these techniques are either expensive or ineffective for large-scale projects. They also require constant monitoring and tedious control. Hence, bioremediation (biological treatment) is suggested as an environmentally friendly substitute for the successful removal of HMs from polluted sites.

Algae are non-vascular plants that range in size from single-celled or colonial microalgae or “phytoplankton” such as diatoms and dinoflagellates, to large multicellular macroalgae such as seaweed or kelp [25]. Every alga contains chlorophyll but the majority of them lack stems, vascular tissue, roots, and leaves [25]. Bioremediation by algae, called “phycoremediation”, has emerged as a viable method for removing HMs from wastewater [26–28]. Phytoremediation is the process of using plants to sequester toxic chemicals from soil and water [29,30]. Advantages of using phytoremediation include: economic feasibility—phytoremediation is an autotrophic system driven by solar energy, hence their management is easy, and the maintenance and installation cost is low; eco-friendly—it can decrease the exposure of the contaminants to the ecosystem; applicability—it may be used over a vast field and may be disposed easily; it checks leaching and erosion of metal by stabilizing HMs, decreasing the risk of proliferation of contaminants; it may also improve the fertility of soil by releasing several organic matters into the soil [31–33]. Advantages of phycoremediation (Figure 1) include economic viability [34]; algal biomass may be used over a period of years [35]; algae have the potential to sequester diverse contaminants (e.g., HMs, pesticides, inorganic and organic toxins) [36]; in dilute effluents, they are quite effective, due to their high surface area-to-volume ratio [37]; they are highly efficient at sequestering HMs [36]; they are suitable even in wastewater containing higher metal concentrations [37]; algae are appropriate for aerobic and anaerobic effluent treatment units [38]; and cultures of microalgae may be cultivated in large-scale reservoirs, open ponds, and also in the laboratory [38].



**Figure 1.** Multiple benefits of growing algae in wastewater.

### *Other Ecosystem Services of Algae*

Algae play a crucial role in aquatic ecosystems by constituting the energy base of the food web for all the aquatic fauna. As autotrophic organisms, algae transform  $H_2O$  and  $CO_2$  to sugar by the process of photosynthesis [39]. Photosynthesis also produces oxygen as a by-product, helping in the survival of fish and other aquatic fauna. Algae are significant components of various biogeochemical cycles and are important members of aquatic environment food webs [40]. Furthermore, algae also harm several goods and services of the ecosystem [41]. Hence, algae may be employed to signify ecosystem goods and services that complement how algal indicators are also used to measure the pollutant levels and habitat changes [42].

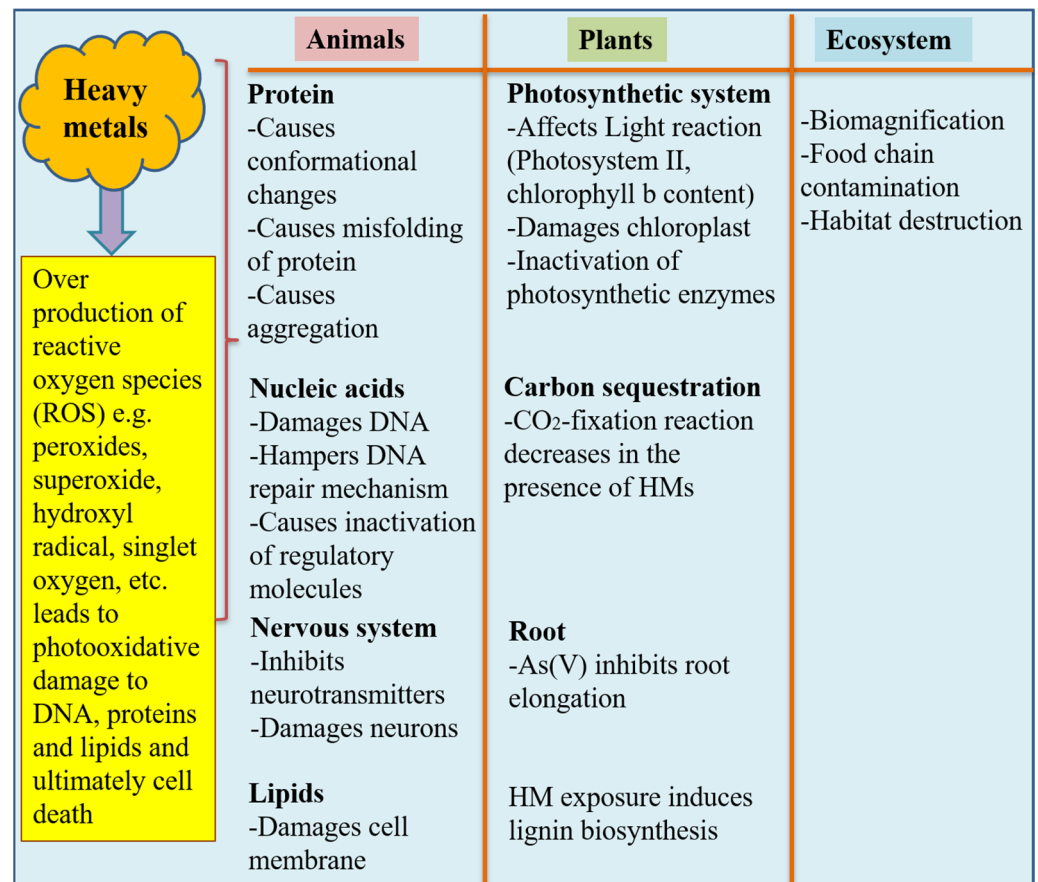
Algae affect the quality of water, assist in sewage treatment, and generate biomass [43]. They may be employed to produce hydrogen, which is a clean fuel, and biodiesel. Few other ecosystem services include decreasing the  $CO_2$  load of the atmosphere, restoring contaminated ecosystems, global warming mitigation, etc. [44–46]. Algae may be important in understanding and fixing some environmental issues [47,48].

Algae are known to be an excellent renewable energy source due to their fast rate of growth and their capability to be grown in wastewater or waste land [49]. Many government agencies and industries are making efforts to reduce the operating costs and capital cost, and to make algae-based fuel production economically feasible [50]. Algae are fast-growing plants that can produce more biomass or oil per acre than other plants and crops. Algal lipids would be one of the best feedstocks because they have the capacity to sequester enormous volumes of  $CO_2$ , and do not compete heavily for agricultural land or food prices (i.e., the “food vs. fuel” concern is not relevant). Biofuels, which principally include biodiesel, biogas, and bioethanol, have come a long way and are likely to become important sources of sustainable energy in the future [51].

The buildup of HMs by algae offers various advantages for phytoremediation over other, less cost-effective and environmentally friendly approaches. This review looks at how algal biomass may help remove HMs from water and wastewater. High HMs ion uptake capacity and low-cost cultivation, with appropriate environmental conditions such as time, pH, temperature, and contact, make algal biomass very useful for wastewater bioremediation. The review’s purpose is to offer an overview of HMs as a potential contaminant in aquatic ecosystems, the phytoremediation potential of algae, and the underlying mechanism of HMs accumulation.

## **2. Heavy Metal as a Potential Contaminant of Aquatic Ecosystems**

Aquatic ecosystem contamination with HMs has escalated since the inception of the industrial revolution. In contrast to organic chemicals, most of HMs cannot break-down into less toxic or non-toxic compounds [52]; hence, they may persist in the aquatic ecosystems. HMs present in bioavailable form may be accumulated by aquatic life and, in due course, move up the trophic levels [52]. Upon entering the biological systems, HMs may interfere with development, growth, and metabolism, leading to several chronic and severe effects [53]. Few HMs are nutritionally important at lower levels, e.g., copper (Cu), zinc (Zn), and iron (Fe), whereas others do not contribute to biological functions, e.g., Pb, mercury (Hg). Nevertheless, surplus exposure of HMs may lead to toxic effects (Figure 2) [54]. Hence, to ameliorate human and ecological health risk, efforts for remediation of HMs pollution need large-scale implementation.



**Figure 2.** Deleterious effects of HMs [3,55–57].

The majority of inorganic pollutants comprise highly toxic metals (Pb, Cd, Zn, Hg, etc.), whereas few are non-metallic compounds of inorganic nature such as phosphates and nitrates. However, these are still damaging to the aquatic habitat and somewhat toxic to the biological system [12]. HMs have been known to attack cell organelles and components such as mitochondria, cell membrane, nuclei, lysosome, and endoplasmic reticulum, and a few enzymes that take part in damage repair, metabolism, and detoxification in biological systems [58]. Metallic ions can be associated with cellular nucleic acids and can cause DNA damage, which may cause modulation of the cell cycle, apoptosis, or carcinogenesis [10,15,59,60]. Previous research discovered that the generation of reactive oxygen species (ROS) and stress due to oxidation plays a central role in the carcinogenicity and toxicity of metals such as Cd [61], Cr [62], As [63,64], Hg [65], and Pb [63,66]. Due to their potency of toxicity, Cd, Cr, As, Hg, and Pb, rank among the most significant metals in terms of public health. These are systemic toxins that have been shown to cause various harm to organs, even at low doses. The United States Environmental Protection Agency (U.S. EPA) and the International Agency for Research on Cancer (IARC) have classified these metals as either “probable” or “known” carcinogens to humans [53].

### 3. Major Sources and Adverse Effects of Heavy Metals

The nature of HMs varies extensively in terms of their chemical properties, and HMs are used widely in machines, electronics, and high-tech applications. As a result, they find their way into the food chains of animals and humans from a wide range of man-made sources and from natural sources such as the geochemical weathering of rocks and soil [67]. Primary sources of contamination are landfill leachates, mining wastes, industrial wastewaters, municipal wastewater, and urban runoff, especially from the electronic, metal-finishing, and electroplating industries [68]. Many water bodies have concentrations of

metal that are higher than the standards established to protect humans and other organisms. Metals can be transported with sediments and thus may bioaccumulate in the food chain.

Major sources of HMs that involve anthropogenic activities are waste disposal, agriculture, industry, etc. [69]. Nonpoint sources of pollution such as the unregulated release and disposal of domestic and industrial wastewater adversely affects organisms in aquatic ecosystems [70]. Even non-significant concentrations of HMs pose noticeable problems in fauna and flora [71]. HMs do not participate in the metabolism, but they are accumulated via several mechanisms that include bioconcentration, biomagnifications, and bioaccumulation [27]. Organisms exposed to HMs have a protective mechanism against HMs toxicity. Following a threshold level, the HMs content causes direct toxicity to aquatic wildlife and vegetation [72].

In aquatic environments, HMs are one of the most frequent contaminants. These metals give rise to a toxicity threat to animals and human beings, even at very low concentrations, and cause severe impacts at higher levels (Table 1). Lead is very toxic and affects the reproductive system, kidneys, and nervous system [73]. Exposure to Pb leads to encephalopathic symptoms and irreversible brain damage. Cd exposure leads to renal problems, liver damage, bone degeneration, and blood-related problems [74]. It has been reported that there is enough evidence that proves the carcinogenicity of Cd. High-level exposure to Cu dust causes irritation in the mouth, eyes, and nose, and can cause diarrhea and nausea. Continuous exposure can cause damage the kidney and even death. Cu is harmful to a variety of aquatic organisms, even in trace amounts [75]. Accumulation of HMs inside the plant cell leads to inhibition of photosynthesis, decreases algal growth, and increases the permeability of the plasmalemma, which leads to loss of cell solutes, breakdown of the of the cell membrane, enzyme inhibition, unusual morphological development, and loss of flagella in certain algae [76].

**Table 1.** Adverse effect of heavy metal on humans and plants. ROS, reactive oxygen species.

| Metal | Adverse Effects                                                               | Reference  |
|-------|-------------------------------------------------------------------------------|------------|
| As    | Carcinogenic effects                                                          | [64,65]    |
|       | Hyperpigmentation, melanosis and keratosis in humans                          |            |
|       | Genotoxic, as it leads to the generation of ROS and causes lipid peroxidation |            |
|       | Immunotoxic                                                                   |            |
|       | Modulates co-receptor expression                                              |            |
| Hg    | Causes Black foot disease                                                     | [66,67]    |
|       | Mutagenic effects                                                             |            |
|       | Minamata disease                                                              |            |
|       | Hampers cholesterol                                                           |            |
| Cd    | This leads to severe bone and kidney damage in humans                         | [68–70]    |
|       | Anemia, bronchitis, emphysema,                                                |            |
|       | Acute toxic effects in children                                               |            |
| Zn    | Causes anemia                                                                 | [71]       |
|       | Phytotoxic                                                                    |            |
|       | Leads to a decrease in muscular coordination                                  |            |
|       | Causes pain in the abdomen                                                    |            |
| Cu    | Phytotoxic                                                                    | [65]       |
|       | Damages a range of aquatic fauna                                              |            |
|       | Corrosion and mucosal irritation                                              |            |
|       | Disturbs the central nervous system and can lead to depression                |            |
| Cr    | Irritates gastrointestinal mucosa                                             | [72]       |
|       | Nephritis and death in humans at higher doses of Cr (VI)                      |            |
| Ni    | High concentration may lead to DNA damage                                     | [65]       |
|       | Negative effect on fauna                                                      |            |
|       | Causes phytotoxicity                                                          |            |
| Pb    | Phytotoxic                                                                    | [66,73,74] |
|       | High concentration may lead to metabolic poison                               |            |
|       | Toxic to humans, aquatic fauna and livestock                                  |            |
|       | Hypertension leading to brain damage                                          |            |
|       | May lead to fatigue irritability, anemia and behavioral changes in children   |            |

#### 4. Phytoremediation Potential of Algae

Algae have similar photosynthetic pigments as those of higher plants but algae have greater photosynthetic efficiency, and algae release higher amounts of oxygen into water bodies, leading to aerobic breakdown of organic compounds [77]. Algae utilize waste as a source of nutrition and decrease pollutants by enzymatic and metabolic processes. HMs pollution and xenobiotic compounds may be volatilized, detoxified, and transformed by the algal metabolic pathways [78].

Mechanisms for removal of HMs include flocculation, absorption, sedimentation, precipitation, cation and anion exchange, microbiological activity, oxidation/reduction, and uptake and complexation [79]. Removal of HMs by microalgae is performed directly via two major mechanisms; one is metabolism, which is dependent on the uptake of HMs in cells at low concentrations, and the other is biosorption, which is a passive process of adsorption [80].

Phytoremediation is the process of remediating soil and aquatic systems with the help of plants, algae, or fungi to absorb HMs. Lately, the application of macro- and microalgae has drawn significant attention because of their capability to sequester toxic elements from the environment [81].

Algae possess various characteristics that make them excellent candidates for selective HMs removal, including include the ability to grow heterotrophically and autotrophically, high surface area/volume ratios, tolerance to HMs, phototaxy, and genetic manipulation potential and phytochelatin expression [82]. *Cladophora* and *Enteromorpha* have been used to monitor levels of HMs [83]. Macroalgae have been used widely monitor HMs contamination in marine environments.

The propensity of macroalgae to collect metals inside their tissues has led to their widespread usage as metal availability bioindicators [84–86]. *Cyanophyta* and *Chlorophyta* are hyper-accumulators of As and B [87], absorbing these metals from the contaminated ecosystems. These algae may be efficient phycoremediators and their presence in water may decrease As and B [87]. The Phaeophyta are promising accumulators of metals because of the presence of significant levels of alginates and sulphated polysaccharides inside their cell walls, for which metals have high affinity [88]. Nielsen et al. [89] observed that brown algae such as *Fucus* spp. sometimes dominate the vegetation of HM-contaminated habitats.

Microalgae are microscopic, aquatic organisms that thrive in both marine and freshwater environments, and have a mechanism of photosynthesis that is similar to that of land plants. Biomass-wise, they constitute the biggest group of primary producers, accountable for almost 50% of global photosynthesis [90]. They have molecular processes that distinguish between essential and unnecessary HMs for growth [91]. Researchers have widely focused on the benefits of using microalgae in the biosorption of metals. The advantages include: fast capability to uptake metal (compared to higher plants), saves time and money, environmentally friendly, ready availability, perpetual occurrence, reusable/recyclable, efficient, high surface-to-volume ratio, capability to bind as much as 10% of their biomass with increased selectivity (which increases their performance), no generation of toxic waste, advantageous in both continuous and batch systems, and employable to waters having variable concentrations of metals and other contaminants [92]. Monteiro et al. [92] supported the importance of microalgae in removing metals, even at trace amounts of contamination. Microalgae not only have a better efficacy for HMs remediation, but they also help with HMs recovery using only some basic desorption compounds. They can remediate HMs from multi-metal solutions [93,94]. Rajamani et al. [94] described the transgenic methods employed to increase the HMs binding capability of microalgae, including the application of fluorescent HMs biosensors devised by employing transgenic *Chlamydomonas*. Microalgal affinity for polyvalent metals aids in determining its potential application in purifying wastewater having dissolved metallic ions [95]. *Chlorella* and *Scenedesmus* are the microalgae of choice for metal removal. Brinza et al. [96] studied the ability of *Chlorella salina*, *Chlamydomonas reinhardtii*, *C. vulgaris*, *Chlorella sorokiniana*, *Chlorella miniata*, *Scenedesmus quadricauda*, *Scenedesmus abundans*, *Spirogyra* spp., *Scenedesmus*

*subspicatus*, *Spirulina platensis*, *Stigeoclonium tenue*, *Stichococcus bacillaris*, and *Porphyridium purpureum* to absorb metals such as Al, Ca, Mg, Fe, Co, Cu, Sr, Pb, Mn, V, Ni, Cd, Se, Zn, Mo As, and K. [96]. Perales-Vela et al. [91] studied Cu, Cd, and U removal capabilities of *P. tricornutum*, *Scenedesmus* and *Chlorella*. They found that microalgae synthesize peptides can bind to HMs [91], resulting in the formation of organometallic complexes that are further positioned within the vacuoles to make it easier to manage the cytoplasmic concentration of HMs ions, nullifying the HMs' potential harmful effects [97].

The marine alga *Dunaliella tertioleca* exhibited high content of phytochelatin attributed to its ability to hyperaccumulate Cd and Zn [98]. Rhodophyta, Chromophyta, and Chlorophyta have strong cytochrome P<sub>450</sub> monooxygenase activity and are efficient against xenobiotic (foreign) substrates such as 2,3-dichlorobiphenyl, isoproturon and 3,4-chlorobiphenyl [99,100]. The action of Nitroreductases on nitroaromatic compounds such as Glycerol trinitrate (GTN), 2,4,6-trinitro toluene (TNT), and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in some was indicated by several researchers who successfully used transgenic approaches to produce end-products such as nitrate, ammonium, and CO<sub>2</sub> [100,101]. Scientists discovered an mt gene in the marine brown alga *Fucus vesiculosus* that was activated with Cu exposure, and the proteins produced efficiently bound to Cu and Cd [102]. Several species of algae have been extensively studied and found to bear excellent potential to remove HMs from contaminated water (Table 2).

**Table 2.** Heavy metal removal potential of algal species.

| Algae                                                                                 | Metal Removed                       | Description of Metal-Rich Surrounding | References |
|---------------------------------------------------------------------------------------|-------------------------------------|---------------------------------------|------------|
| <i>Anacystis nidulans</i>                                                             | Cu                                  | Solution of metal                     | [103]      |
| <i>Tolypothrix tenuis</i>                                                             | Cd                                  | Aqueous solution                      | [104]      |
| <i>Synechocystis</i> sp., <i>Scenedesmus obliquus</i> , and <i>Chlorella vulgaris</i> | Cr (VI), Ni, Cu                     | Aqueous solution                      | [105]      |
| <i>Nostoc muscorum</i>                                                                | Cd and Cu                           | Multi metal solution                  | [106]      |
| <i>N. rivularis</i> and <i>Nostoc linckia</i>                                         | Cd and Zn                           | Sewage water                          | [107]      |
| <i>Chlorella vulgaris</i>                                                             | Ni and Cu                           | Single and binary metal solution      | [108]      |
| <i>Spirulina</i> sp.                                                                  | Trace element                       | Copper smelter and refinery effluent  | [109]      |
| <i>Aulosira fertilissima</i>                                                          | Ni and Cr                           | Free-cell condition                   | [110]      |
| <i>Anabaena</i> , <i>subcylindrical</i> , and <i>Nostoc muscorum</i>                  | Mn, Co, Pb and Cu                   | Industrial wastewater and sewage      | [111]      |
| <i>Cladophora fascicularis</i>                                                        | Pb and Cu                           | Aqueous solution                      | [112]      |
| <i>Spirulina platensis</i> (Spi SORB)                                                 | Cu                                  | Column reactor system                 | [113]      |
| <i>Chroococcus</i> sp. and <i>Nostoc calcicola</i>                                    | Cr                                  | Metal-contaminated soil               | [114]      |
| <i>Gloeocapsa</i> and <i>Lyngbya</i>                                                  | Cr                                  | Contaminated sites                    | [115]      |
| <i>Aphanothece flocculosa</i> and <i>Spirulina platensis</i>                          | Hg                                  | Wet biomass                           | [116]      |
| <i>Gloeotheca</i> sp. strain PCC 6909                                                 | Cu                                  | Wastewater                            | [117]      |
| <i>Hapalosiphon welwitschii</i> Nägel                                                 | Cd                                  | Metal solution                        | [118]      |
| <i>Phormidium</i> sp. NTMS02 and <i>Oscillatoria</i> sp. NTMS01                       | Cr (VI)                             | Aqueous solution                      | [119]      |
| <i>Caulerpa racemosa</i> and <i>Sargassum wightii</i>                                 | Cd, Pb, Cr (III and VI)             | Aqueous solution                      | [120]      |
| <i>Caulerpa lentillifera</i>                                                          | Cu (II), Pb (II), Cd (II),          | Aqueous solution                      | [121]      |
| <i>Sargassum</i> sp                                                                   | Cu (II), Cd (II), Ni (II), Fe (III) | Aqueous solution                      | [122]      |
| <i>Gelidium</i> sp.                                                                   | Pb (II), Cu (II), Cr (III)          | Aqueous solution                      | [123]      |

Table 2. Cont.

| Algae                       | Metal Removed                      | Description of Metal-Rich Surrounding | References |
|-----------------------------|------------------------------------|---------------------------------------|------------|
| <i>Ulva reticulat</i>       | Cu (II), Co (II), Ni (II), Zn (II) | Aqueous solution                      | [124]      |
| <i>Posidonia oceanica</i>   | Cu (II)                            | Aqueous solution                      | [125]      |
| <i>Sargassum baccularia</i> | Cu (II)                            | Aqueous solution                      | [126]      |
| <i>Ulva lactuca</i>         | Cu (II), Zn (II), Cd (II), Pb (II) | Aqueous solution                      | [127]      |

Mei et al. [128] observed that *Platymonas subcordiformis*, a marine green microalga, is a hyperaccumulator of Sr (strontium). However, high Sr concentration leads to oxidative damage, as suggested by the surge in lipid peroxidation in the cell samples of algae and the decline in the chlorophyll contents and rate of growth. Few species of algae can convert phenylmercuric or mercuric ions into metallic mercury, which is then volatilized out of the cell and from the solution [129,130]. *Phormidium*, a blue-green alga (which are actually procaryotes), is a promising hyperaccumulator of HMs such as Zn, Cd, Pb, Cu, and Ni [131,132]. *Caulerpa racemosa* is a cheap biomaterial that could be used for removing boron (B) from contaminated water bodies [133,134]. *Dunaliella salina* (green microalgae) is a promising accumulator of Zn followed by Cu and Co, and the lowest accumulation was for Cd. This can be due to the significance of Zn as a hydrogen transporter in the process of photosynthesis [134]. Metallic cations form complexes with carboxyl and other functional groups in algae. Further research may reveal that some algal species have adsorption capacities for different HMs [135].

## 5. Mechanism of Phytoremediation by Algae

Many researchers have documented the capability of phytoplankton to take up HMs from water bodies [136–139]. Removal of HMs ions by microalgae occurs through biosorption and bioaccumulation.

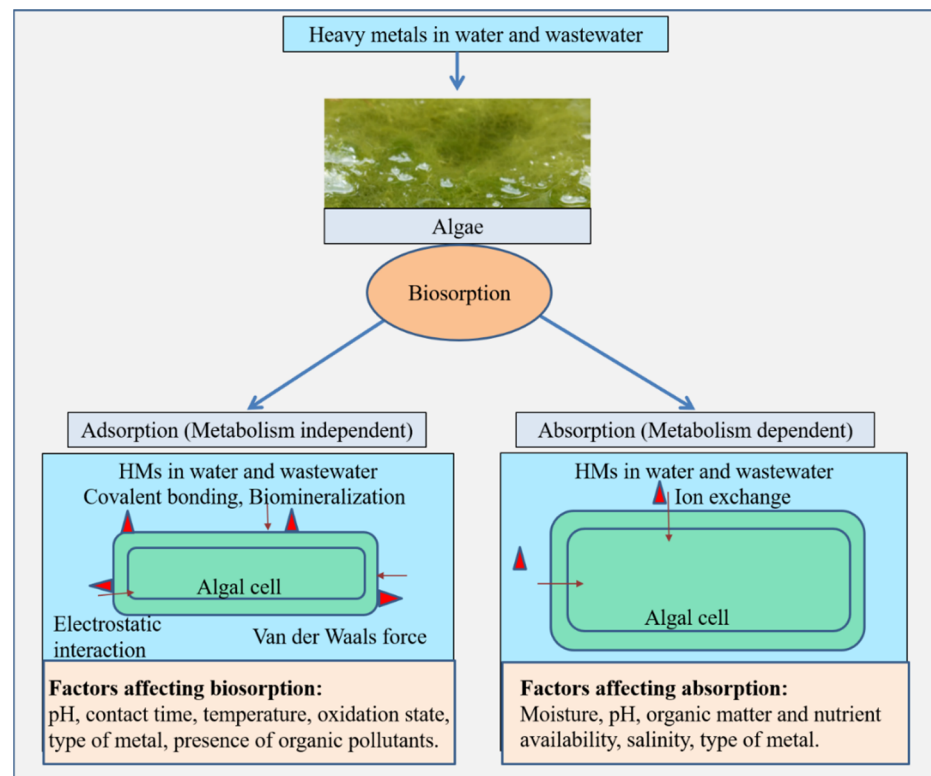
### 5.1. Biosorption

In biosorption, HMs ions adhere to functional groups on the cell surface (Figure 3) [140,141]. Algal cell wall components such as fucoidan and alginate are the most important functional groups accountable for HMs biosorption [142,143]. HMs ions in wastewater are exchanged with elemental ions such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{K}^+$  on the surface of algae. The feasibility of this process is contingent upon critical factors such as regeneration potential and metal selectivity. Chemical modification of the algal biomass, such as oxidation with potassium permanganate or crosslinking with epichlorohydrin, improves biosorption selectivity [144].

Biosorption is a physio-chemical property that results in removal of HMs by covalent or ionic bonding [145,146]. Various functional groups, such as  $\text{SH}^-$ ,  $\text{COO}^-$ ,  $\text{RNH}_2^-$ ,  $\text{RS}^-$ ,  $\text{RO}^-$ , and  $\text{OH}^-$ , facilitate metal ion biosorption. These groups can be present on the cell surface and in the cytoplasm, particularly in vacuoles. Algal cell walls have a net negative charge because of the presence of  $\text{PO}_4^{3-}$ ,  $\text{COO}^-$ , and other functional groups that bond with metals through ion exchange. *Ditylum brightwellii* and other species of algae produce a special material known as Cu-ligands [146,147]. Carboxyl ( $\text{COO}^-$ ) present in brown algal cell walls is the most profuse acidic functional group. Algae minimize damage induced by metals through exclusion and excretion of metals and by synthesizing proteins and other binding compounds such as glutathione (GSH) and metallothioneins (MTs) [147,148]. Other functional groups are found in algae with different cell wall compositions. The selectivity of HMs uptake is contingent upon the encapsulation of microalgae and its cellulose derivatives [147,149]. Desorption of the adsorbed HMs can occur at a lower pH of suspension. Reversible loading or unloading of adsorbed HMs is achievable by utilizing citric acid or HCl sorption. Experiments on biosorption of metals have been conducted with brown algae (e.g., *Fucus vesiculosus* and *Laminaria japonica*), blue-green algae (e.g., *Oscillatoria* sp. and *Microcystis aeruginosa*), and freshwater green microalgae

(e.g., *Scenedesmus* sp., *Chlorella* sp., and *Chlamydomonas* sp.) [150]. Several technologies for the removal of HMs, including algal turf scrubbers and high-rate algal ponds, have been backed for pragmatic usage. These technologies, however, are currently insufficient for large-scale implementation. Success of phytoremediation is dependent primarily on the bioaccumulation and biosorption capabilities of the algae, with biosorption controlling bioremediation [151]. Algae are economical and efficient biosorbents because of their low nutrient requirements. Algal biosorption effectiveness is around 15.3–84.6% higher than that of other fungi and bacteria [142,152,153].

The ability of algae to metabolize and adsorb HMs is linked with their high surface-to-volume ratios, efficient metal uptake, storage systems, and the presence of high-affinity metal-binding groups on their cell surfaces [27]. In physical adsorption, metal ions in aqueous solution bind to polyelectrolytes on the algal cell wall through weak forces such as redox interaction, covalent bonding, biomineralization, and van der Waals forces [154]. The pH of the adsorbing media strongly influences adsorption of metal ion. By replacing the functional groups on metal cations, alkaline pH boosts their attraction and eventually increases their adsorption on cell surfaces that carry a negative charge, such as phosphate, polysaccharides, aminos, carboxyl groups of protein, and amino groups of nucleic acid [75].



**Figure 3.** Phytoremediation mechanism of algae.

## 5.2. Bioaccumulation

By the process of bioaccumulation, HMs ions are transported across cell membranes through passive and active transport systems and accumulate inside the cells. Extracellular and intracellular metal binding approaches (such as complexation, physical adsorption, ion exchanges and chelation) have been employed by algae to lessen toxicity caused by HMs [155].

These mechanisms efficiently transform toxic metals into less or non-toxic forms [153,155]. Detoxification of metal by algae is performed in various ways such as binding to a particular intracellular organelle, transport to particular cellular components such as polyphosphate vacuoles/bodies, flushing out into the solution by efflux pump, and with synthesis of class III metallothioneins or phytochelatins [91,156]. Phytochelatins are peptides that bind

to metals and are small, having molecular weights in the range from 2 to 10 kDa. Phytochelatins are synthesized by the constitutive enzyme called phytochelatin synthase [157]. Their synthesis from g-glutamylcysteine, hydroxymethyl-glutathione, homo-glutathione or glutathione [158] is catalyzed by a trans-peptidase known as phytochelatin synthase (the constitutive enzyme) that needs post-translational activation by HMs [159,160]. All higher plants and most algae can synthesize phytochelatins [161]. Cobbett and Goldsbrough (2002) conducted kinetic studies demonstrating that the synthesis of phytochelatin is quick (within a few minutes) and is not dependent on de novo synthesis of protein [162]. A diverse range of metalloids and metals such as As, Cu, Cd, Pb, Ag, Sn, Hg, Zn, and Au may help in activating phytochelatin synthase both in vivo and in vitro [163]. Cd was found to be a potential activator of phytochelatin synthesis and was able to promote the synthesis of phytochelatins with more stable chains (i.e., up to PC<sub>5</sub>) [163,164].

Precipitation in sulfide, phosphate, or carbonate reduces HMs toxicity on living algae. *Cladophora glomerata*, a green alga, was capable of removing Pb, Cd, Ni, Cr, and V at 7.9, 0.1, 15.6, 1.7, and 37.7 mg kg<sup>-1</sup>, respectively, from a refinery sewage lagoon [147]. *Fucus vesiculosus*, a brown macroalga, exhibited a significant efficiency for HMs accumulation from contaminated saltwater, removing 65, 95, and 76% of Pb, Hg, and Cd, respectively. Bioconcentration factors for Cd, Pb, and Hg ranged from 600 to 2300, with complete metal removal from the solution [165].

## 6. Conclusions

HMs contamination of aquatic ecosystems is a serious concern because of its toxicity towards human health and all biota. Several species of algae have been identified as promising candidates for removal or detoxification of HMs and are potential economical substitutes to physicochemical techniques of remediation. Removal of HMs can be attained by bioaccumulation and biosorption. Microalgae, predominantly, possess several mechanisms for sequestering HMs ions and are therefore recognized as potential biosorbents. Many reports corroborate their supremacy over several other physiochemical and traditional methods and their usefulness in large-scale remediation of wastewater. Although algae have excellent potential to be used for HMs accumulation, they have some limitations such as low biomass, and sensitivity towards high concentration of HMs. These problems may be solved by some advanced interventions such as genetic modifications that enhance the biomass production. In addition, in the field, a suitable and sustainable method for selecting the most acceptable biosorbents and favorable physical circumstances, and identifying the primary problems, must be developed. However, it is critical to consider a variety of microalgal remediation methods as environmentally acceptable alternatives for a healthier environment. Genetic engineering can be used to enhance the creation of transgenic organisms that over-express phytochelatins and metallothioneins that can form complexes with HMs and translocate them into vacuoles, and aid phytoaccumulation and hazardous element removal from aquatic habitats. Microalgae strains show varied response and tolerance along with bioaccumulation capability towards HMs. Various functional groups and proteins, in addition to peptides, are accountable for metal-binding. Mechanisms such as volatilization, reduction, extracellular adsorption, complex formation, intracellular accumulation, bio-methylation, and ion exchange chelation are involved in bioremediation and biosorption of HMs. More efforts in the areas of immobilization techniques, genetic engineering, and integration, along with other techniques, are required to entirely explore the potential of microalgae in HMs phycoremediation and, simultaneously, the formation of value-added products.

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