



RESEARCH ARTICLE

Bioremoval of Heavy Metals in Water by Algal Biotechnology: A Review

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ABSTRACT

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Pollution of water sources with heavy metal (HM) is a critical issue facing the environment on a worldwide scale. They are non-biodegradable, which means that they could accrue in food chains, causes different symptoms of toxic to subject organism, involving humans. As a result, some algae, in particular, have developed effective methods to collect these toxic metallic and capture there. These natural processes can potentially eliminate specific toxic metals from the surrounding environment. Additionally, the effect of abiotic parameters on removing HMs, including pH, temperature, and ion strength, will be examined. Specifically, microalgae have been identified as ideal carries for detoxifying and found as viable low-cost alternate to physicochemical therapies. This recognition came about as a result of the fact that microalgae are very abundant. The process of live microalgae "adsorbing" metals onto their surfaces occur in two stages: the first step happens very quickly and is mostly unaffected by the cell's metabolic processes; this stage is called "adsorption." The second one is more involved and depends on the cell's metabolism; this process is known as "bioaccumulation" or "intracellular uptake." In addition, by using cells that are not viable, the elimination of metals from polluted locations has been accomplished. According to several studies, the primary factor of the biosorption of heavy metal ions is thought to be the elements of the cell walls of algae,, which involve important functional sets. This research investigates the processes responsible for the bio-remediation of hazardous metals (HMs) by microalgae.

INTRODUCTION

Heavy metals (HMs) are the source of surface and water pollution, which is a major reason for worry on a worldwide scale [1]. HMs in wastewater may be attributed to several naturally occurring events (including volcanic or another eruptions) and man-made activities (eg discharges of industrial solid and effluents). Varied sectors, including mining, dyes, textiles, electroplating, battery production, vehicle manufacturing, and many more, are responsible for discharging HMs into the environment [2]. Toxic metals are discharged into the air and soil by these businesses, eventually making their way into bodies of water, according to [3]. HMs including gold, silver, boron, cobalt, iron, manganese, nickel, zinc, copper, molybdenum, cadmium, titanium, chromium, nickel, arsenic, lead, and mercury, amongst others, when they move inside the food chain and cumulative in to the human body, have a negative impact not only on ecosystems but also on human health. HMs can be found in various foods [4,5,6].

HMs are well recognized as one of the most dangerous toxins that contribute to environmental degradation on a global scale. The buildup of these substances in the environment ultimately results

in biomagnification [7]. These are not biodegradable in any way, and negatively influence the environment as a whole. HMs are employed without consideration for human dangers which results in a disruption of the biogeochemical cycles. The presence of HMs over the allowed levels in the earth's soil, air, and water has a negative impact on the planet's diverse ecosystem and may be endanger to individual health [8,9]. In addition, HMs are a major contributor to the development of respiratory, renal, mental, and cardiovascular problems, as well as cancer [10]. Deleterious effects of HMs for animals, plants and ecosystem, explain in (Table 1) [11,12,13]. For this purpose, the pertinent universal establishments have provided instruction on accepted values for maximum heavy metal pollutant scales in water and wastewater, shows in (Table 2) [14,15, 16,17].

Heavy metals can be classified into three categories, which are as follows: i) very poisonous HMs, involving tin, cobalt, arsenic, cadmium, nickel, copper, zinc, lead, mercury, and cadmium. (ii) valuable metals, most often involving Pd, Pt, Ru, Au, and Ag; (iii) radionuclide HMs, involving Th, Ra, U, and Am; and (iv) rare earth elements. Furthermore, even at very depress concentrations, on-essential HMs exhibit variable grades of toxication with regard to microbes, animals, vegetations and people [18]. The case is even when the HMs are in trace amounts [7]. As a result, the remediation of water that is polluted with HMs has become a worldwide concern that has captured the interest of scientists, environmentalists, and politicians. Therefore, these toxins must be eliminated from industrial effluent and aquatic habitats to defense the habitats and public soundness.

Table 1: Deleterious effects of HMs for animal, plants and ecosystem.

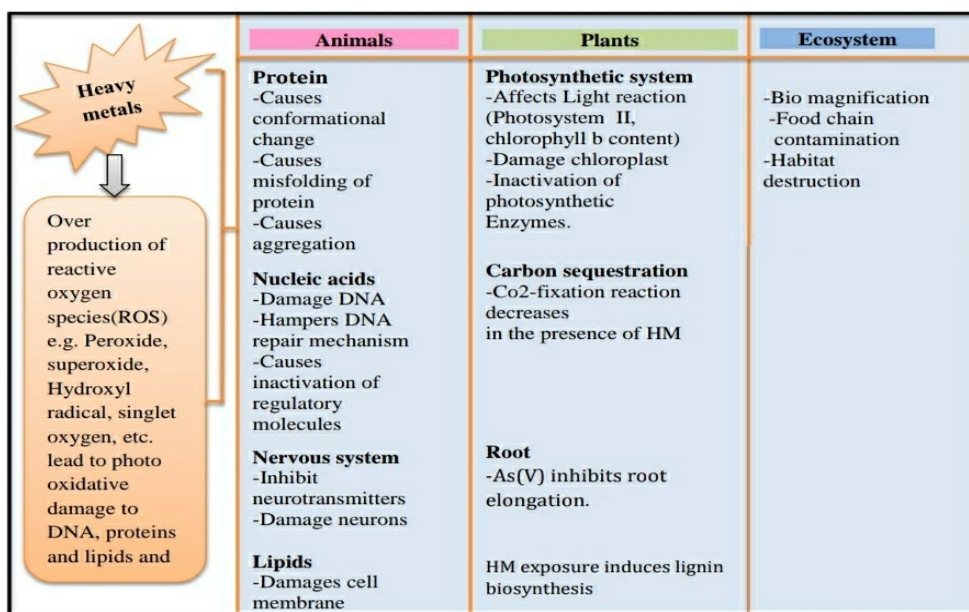


Table 2: Allowable levels of heavy metals in the water.

Heavy metal	Allowable levels (mg/L)		industrial wastewater sources	Impact human health
	WHO	EPA		
Mercury	0.01	0.05	the medicine materials, papers, pulp, ore, battery	Neurological diseases, paralysis, blindness
Lead	0.05	-	Battery, pipe, ceramic, glass production	Brain damage, anemia, anorexia
Arsenic	0.01	0.05	Glass, mining, textile, paper, insecticides, phosphate fertilizers, mining, coal combustion	Lung and kidney cancer, liver tumors, nausea

Copper	1.0	0.25	Fertilizer, pigments, tannery paints,	Liver and lung cancer, insomnia, osteoporosis, heart disease, headaches, seizures
Cadmium	0.003	0.005	Fertilizer, battery, power plants, mining, smelting, fuel combustion	lung cancer, kidney failure, bone lesions.
Chromium	0.05	0.05Cr(VI) 0.1 Cr(III)	Synthetic dyes, steel production, textile, ceramic	Lung cancer, hemorrhage, vomiting, severe diarrhea
Nickel	0.015	0.2	Battery, mining, coinage, electroplating, glass, paints	Lung cancer, dermatitis, chronic asthma
Zinc	3.0	1.0	Mining, steel fabrication, galvanization, stabilizers, coal combustion	Gastrointestinal disorder, nausea, lethargy, neurological damage, loss of appetite

Heavy metal elimination in wastewater is accomplished using conventional and contemporary methods. Conventional methods, that include ion exchange, electrochemical treatment, osmosis, evaporation, and precipitation, demand greater energy input, resulting in higher costs. In addition, most of these approaches provide issues about the elimination of metals from the environment in a sustainable manner [19, 20]. To get around this problem, contemporary approaches including biological procedures, which are more cost-active and environmentally friendly to heavy metal elimination, are used [21]. At the same time, these procedures are simple to implement and come highly recommended as an alternative strategy that is kind to the environment and can effectively remove HMs from locations that have been polluted [22].

The process of removing contaminants from the water via algae is called phytoremediation. Because algae are readily accessible, affordable, have great metal elimination capability, are environmentally benign, and give birth to value-added products, this approach can be used to reduce HMs. The biosorption and bioaccumulation eliminate most contaminants, and detoxifying technique established for algae throughout the phytoremediation process. In the biosorption operation, toxic metals' sorption onto the surface of the biomass happens in any case whether the mass live or dead cells [23]. Through of the process bioaccumulation, HMs are moved about within the algae cells. During the process of detoxification, certain phytochelatin that are generated via algae assist in the transformation of poisonous toxic metals into a substance that is not hazardous [24].

It has been demonstrated that bioenergy derived from algae is the most sustainable and environmentally beneficial kind of energy [25].

In order to make phytoremediation a sustainable process, the biomass harvested throughout the process may be put to use in the manufacture of bioenergy as well as several other high-value products [26].

In addition to elimination of the HMs in the wastewater, it may also create environmentally friendly method. Phytoremediation has many usefulness over other bioremediation methods, involving the following: (1) biomass of algae can be implemented in wastewater with a high concentration of metals than the membrane method [27]; (2) there is no requirement to synthesize algal mass; (3) It can be reused and regenerated in many adsorption/desorption chains; (4) Capacity of high absorption and effective elimination of HMs [28]; (5) there is no toxic chemical produced sludge (6) algal don't need way to be immobilized them (7) algae may be employed in both continuous and discontinuous

regimes; (8) while employing non-living biomass, there is no need for the delivery of nutrients or oxygen; (9) suitable for both anaerobic and aerobic wastewater remediation portions; (10) biomass of algae may be utilized continuously throughout the year [29]; and (11) economical [30].

1-Heavy Metal as a Potential pollution of Aquatic Ecosystems

Urbanization and industrialization are responsible for environmental contamination in the air, water, and soil. There are several types of pollutants, such as organic, inorganic, metallic, gaseous and biological pollutants, which contaminate the environment [31]. Contamination from metallic ions in water arises due to several natural and anthropogenic activities, which harm animals and plants [32]. Several industrial processes, including leather tanning, chrome plating, battery manufacturing, the glass industries, agricultural activities, domestic waste, and pharmaceutical industrial processes, are considered major sources of heavy metals, which generate toxic metal ions in the environment [33]. Heavy metals including arsenic (As), chromium (Cr), lead (Pb), and cadmium (Cd) are toxic to humans [34]. The biological removal of heavy metals is more appealing than other conventional methods, because biological methods are cost-effective, eco-friendly, and efficient when removing low concentrations of heavy metal ions from wastewater [35]. Several heavy metal bioremediation methods, including biosorption, phytoremediation, bioreduction (the conversion of oxidation states of heavy metal ions), and bioaccumulation (the uptake of heavy metal ions into intracellular space) have been proposed in past, heavy metals can be remediated using metabolically independent (dead materials) and metabolically dependent (live cells of bacteria, fungi, and algae) agents [36].

2-Mechanism of Phytoremediation by Algae

The use of algae in cleaning up polluted wastewater is an example of phytoremediation, which means "phytoremediation" [37]. For microalgae, micronutrients involve a wide variety of HMs including boron, cobalt, iron, manganese, nickel, zinc, copper, and molybdenum. Boron is also a micronutrient. Because they are necessary for the cell's metabolism, these trace elements contribute to the proliferation of algal cells [38]. On the other hand, microalgal development is hindered by poisonous toxic substances including arsenic, lead, cadmium, titanium, mercury, aluminum, gold, and silver. These HMs are not regarded to be advantageous [37]. Studies conducted in great detail on the physiochemical makeup of algal cells shed light on algae's utility in managing environmental contamination, particularly in removing HMs from wastewater used in households and industries. A few algae have demonstrated remarkable tolerance and survivability in water contaminated with extreme heavy HMs [30] due to, its excellent endurance, which allows them to grow easily, have a high bind affinity, have a large surface area, be environmentally friendly, reusable. Dead biomass could be utilized for remediation, which means that no nutrients or other parameters are needed and that the process is act intensive [39,29]. They defend themselves against HMs via various defense mechanisms, involving gene regulation, chelating, and other processes. When the pH of algae is lowered using either hydrochloric or citric acid, the desorption phenomenon may be noticed [38].

Because both live and dead algal cells can conduct biosorption of HMs in their environments, polluted water may be cleaned of HMs via either the living cells or the dead algal cells. On the other hand, removing and retaining a greater quantity of metals through bioaccumulation and biosorption processes for a long time is accomplished more effectively by living algae cells than by dead biomass because living algae cells can remove and retain a higher amount of metals. The HMs extraction efficiency of different algae species in different types of wastewater sources, including dairy effluent, electroplating, petrochemical, and municipal.

The capability of phytoplankton to eject of HMs from aqueous habitats has been the subject of several pieces of research and has been certified [40,41]. Two different processes, referred to as biosorption and bioaccumulation, are used by microalgae in order to remove HM ions from wastewater. Biosorption is a distinct metabolism processes that of may take place together in live and dead cells. It is found in both. Due to micro precipitation, chelating, complication, and ion exchange, HM ions could attach themselves to active sets on the cell's surface throughout this mechanism [42,43]. In

opinion several studies, the primary responsibility for the biosorption of HM ions lies with the structural composition of algal cell walls, involving fucoidan and alginate, that contain important functional sets [44,45]. Ion exchange allows the elemental ions kept on cell surface, including Ca^{+2} , K^+ , and Na^+ , to trade places with these HM ions found in the wastewater around algae cell. This process's success is contingent on several crucial criteria, involving metal selectivity and the possibility of regeneration. Because of physicochemical interactions, selectivity in biosorption could be better because of metals ions attach to the cell's surface. Nevertheless, selectivity may be enhanced with chemical alteration of the biomass of algae, including, cross-link oxidation with potassium permanganate or with epichlorohydrin [46]. The process removed by live microalgae for HMs could include extra-cellular and/or intra-cellular bioremediation mechanisms, and the major avenues involved in the bioremediation and reduction of toxicant element are shown in Figure 1 [47,42].

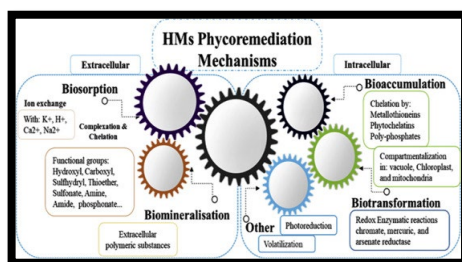


Figure 1: Various mechanisms for the bioremediation by algae.

2-1 Extra-cellular uptake (biosorption)

It is an extra-cellular protection system for the same living organism found in microalgae that blocks the absorption of HMs into the algal cell. This process was detected in microalgae. The surface of cell is where heavy metal uptake takes place, and it is done with the help of functional groups of proteins, lipids, polysaccharides, and monomeric alcohols on the surface of algal cell. These particles have a high concentration of functional sets including phosphate, hydroxyl, and carboxyl [48]. Because these sets all seem anionic, positive-charged metal ions are drawn to them because of their attraction. Ion exchange bonding, covalent bonding and Van der Waal bonding, or any combination of these three types of bonding is responsible for binding these functional sets to positively charged metal ions [49]. Metal absorption differs from strain to strain because each strain has its unique cellular makeup. Algae found in freshwater and marine environments could reduce the amount of HMs including cadmium, zinc, lead, and copper in wastewater by using functional sets like amino, carboxyl, and hydroxyl sets that were present on the cell walls of the algae [50].

When compared to other types of algae, brown algae are proven to be able to detoxify the greatest quantity of HMs. Brown algae have a cell wall of functional sets including alginic acid, cellulose, and other polymers. Researchers [51] found that the (brown algae) *Fucus vesiculosus* can extract zinc from its environment with the presence of hydroxyl and carboxyl sets located on the algal surface. It has been established that the blue-green algae *Anabaena* spherical can remove 121.95 mg/g of lead and 111.1 mg/g of cadmium from a given environment with their assistance of hydroxyl, carboxyl and amino functional sets that are found on the outside cells surfaces [52]. According to [38], it has also been discovered that a decrease of pH protonate the functional set, whose leads to the desorption of HMs and assists in the separation of many different types of economically important toxic metals.

In recent years, the most often employed microalgae strains in the phyto remediation process belonging to the Chlorophyta phylum. More specifically, the strains come from the genus of *Scenedesmus* and *Chlorella* [53]. Despite this, even if the working circumstances are the same, different genera and microalgae species have different sensitivity levels, affecting the biosorption effectiveness [42]. For instance, the development of *Scenedesmus obliquus* and *Chlorella sorokiniana* in a medium polluted with lead (II), cadmium (II), copper (II) and chromium (VI), respectively, was considerably different [54], which may be ascribed to the strain's physiology, namely the cell wall's

composition and structure. With the regard of these phylum, it may range from a basic cell membrane like that of *Isochrysis* and *Dunaliella* species that is made up of a lipid bilayer with peripheral and integrated proteins, to a more complex cell membrane like that of *Euglena*, which is composed of a phospholipid membrane. To greater complex multi-layer structures with extra intra-cellular material contained in vesicles, similar to those seen in dinoflagellate strains [55]. Species that belong to the same genus may have significantly different cell wall compositions although sharing the same genus. *Chlorellavulgaris*, for instance, has an internal layer [56], but *Chlorella zofingiensis* and *Chlorella homosphaera* both have an internal layer, an external layer, and the trilaminar version of the external layer, in addition to having both an internal and an external layer [57]. In the condition of *Chlorella trilaminar*, the layer closest to the surface is made up of sporopollenin, the layer in the center is mostly made up of mannose and chitin-like polysaccharides, and the layer closest to the surface would be a phospholipids bilayer [58].

Ions involving K^+ , Ca^{+2} , Na^+ , and Mg^{+2} are incorporated into the cell surface of microalgae. Through an ion exchange process, these ions can be reversibly exchange by another hazardous HMs ions in the solution. In turn, electrostatic interactions and the physical forces, namely van der Waals may be regulated to control the physical adsorption process of metal binding into the cell surface.

As a result of their minimal fertilizer needs, algae make excellent biosorbents that are also very cost-effective. It has been reported that the biosorption activity of algae is about 15.3–84.6% greater than the biosorption efficiency of other microbial biosorbents (including bacteria and fungus). This conclusion is based a statistics examination for capacity of algae of biosorption [59, 60, 45].

2-2 Intracellular uptake (Bioaccumulation)

Bioaccumulation, on the other hand, is an independent metabolic route other than the biosorption process. It's a term that refers to the buildup of HMs inside live microalgae cells due to the passage of HMs through the cell membranes of these organisms via active and passive transport routes [61]. It is distinguished by 2 phases that occur one after the other. The first stage is identified by a fast, passive, and non-specified absorption for the metallic ions on the cell wall. After that, either passive or active transport occurs between the plasma membrane and the cell wall to reach the cytoplasm [42]. Method of heavy metals removing inside the algal cell, explain in (Figure 2).

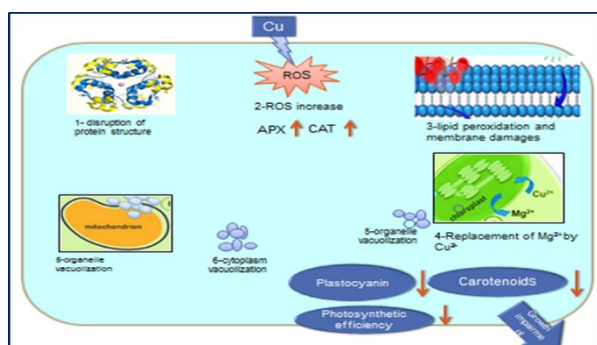


Figure 2: Method of heavy metals such as Cu removing inside the algal cell

Indeed, Researcher [62] found that Cd(II) uptake by *Tetraselmis suecica* was a two-step process. The first step involved Cd(II) adsorption to proteins or polysaccharides. The second step involved the accumulation of Cd(II) in the cytosol in an energy-dependent manner.

Once the content of metal in the extra-cellular environment seems to be substantially greater than the amount within the cell, metal ions could be transferred by the negatively charged sets of the cell surface to achieve the intra-cellular compartment through the use of active transport after binding to thiol molecules, primarily cysteine across the plasma membrane. This process occurs, when the amount of metal in the extra-cellular environment seems to be substantially greater than the amount within the cell [63]. In process of metal chelating and detoxification, additional amino acids, involving histidine,

glutamate, and proline, are also capable of playing an important role [64, 65, 42].

Because of majority of the HMs is hydrophilicity, the transport of these molecules thro plasma membrane (which is lipophilic) is mostly mediated by a particular protein (Metal transporters). After then, different detoxification routes may beoccurring inside the intracellular compartments [66, 67].

On the other words,micro precipitation is a method that is connected with both active and passive routes of metal absorption because micro precipitation involves the formation of microscopic precipitates [68]. Thru precipitation in sulfide, phosphate, or carbonate forms, the detoxification process has the potential to lessen the harmful effects of HM ions on living cells [96].

Ions of metals are stored inside the microalgal cells during bioaccumulation. The process that occurs once those ions begin to collect within the organelles of an algal cell, including the vacuoles or the thylakoids, is referred to as compartmentalization [70]. These processes are sluggish because the process, beginning with the absorption of metallic ions and continuing with transit for those ions interior the cellar among any cell organelles, takes a significant amount of time. Ion-selective transport proteins are located on surface of the cell membranes, and they facilitate the movement of metal ions across the membrane [71]. These activities demand energy for their accumulation, rely on metabolic processes, and could only be carried out by live cells. Only living cells can undertake these processes [72].

Microalgae easily absorb these ions due to their tiny size, which results in a significant ratio of surface area to volume. It has been demonstrated that iron (Fe), nitrogen (N) and sulfur (S),all contribute to the process of bioaccumulation of metal ions [73]. According to the findings of Upadhyay *et al.*, *Chlorococcum* sp. was able to acquire 239.09 g/gfrom the wastewater of arsenic, so, these species can operate as a bio indicator as well as bioremediation. *Tetraselmissuecica*, a species of green algae, was able to bioaccumulation cadmium within the vacuole, while *Skeletonemacostatum*, other green algae, can bio accumulate copperand cadmium of inner part the vacuole [74]. According to observations made by [75], the electron-dense entities into Ulothrix sp. can absorb manganese and nickel. According to research[76], the green algae *Cladophora glomerata* extracted 7.9, 0.1, 15.6, 1.7, and 37.7 mg kg¹ of lead, cadmium, nickel, and vanadium, respectively, from a refinery sewage lagoon. It was demonstrated that the macroalga *Fucus vesiculosus* has a high capacity for accumulating HMs from polluted seawater. In particular, it removed 65% of Pb, 95% of Hg, and 76% of Cd. Bio concentration parameters of lead, mercury, and cadmium varied from 600 - 2300, and every element extracted from the solution was found to have accumulated in the biomass [76].Differences between biosorption and bioaccumulation shows in (Table 3) [77].

Table 3: Comparison between bio sorption and bioaccumulation.

Characteristics	Biosorption	Bioaccumulation
Cost	Usually low. Biomass can be obtained from industrial waste. Cost covers mostly transportation and production of biosorbent.	Usually high. The process occurs in the presence of living cells that have to be supported.
pH	pH of the solution strongly affects sorption capacity of heavy metals. However, the process can occur in a wide range of pH.	Significant change in pH can heavily affect living cells.
Selectivity	Poor. However can be increased by modifications/biomass transformation.	Better than in the case of biosorption.
Rate of removal	Most mechanisms occur at a fast rate.	Slower rate than in the case of biosorption. Intercellular accumulation takes a long time.
Regeneration and reuse	Biosorbents can be regenerated and reused in many cycles.	Due to intercellular accumulation reuse is rather limited.
Recovery of metals	With an adequate eluent the recovery of heavy metals is possible.	If it is even possible, biomass cannot be used for other purposes.
Energy demand	Usually low.	Energy is required for cell growth.

2-3 Biotransformation

Metal detoxification, also known as biotransformation, is kind third of self-protection mechanism demonstrated via micro-algal cells. This process transforms toxic metals into less harmful chemicals with chelators' assistance. Chelating agents are organic chemicals that generate complexes by binding themselves to metal ions and acting as a catalyst for the process. The term "complexation" may also refer to this process. It has been demonstrated that algae secrete chelating compounds as a defense mechanism against the toxicity of metals. These chelating chemicals join with the metal ions, which then causes the ions to transform into a form that is not poisonous [78]. Either these non-toxic complexes were eliminated with the assistance of efflux transporters that are found in the micro algal cell, or these complexes of HMs with other substances are readily stored within cells or another cell organelles (compartmentalization). Chelating substances, including, peptides, thiol-containing compounds, enzymes, organic acids, and many more, are secreted by algae in large quantities [67, 68]. Removal mechanisms of heavy metals by algae, show in (Figure 3).

Peptides including phytochelatin and metallothioneins contribute to the detoxification process carried out by microalgae. Researchers [74] found that the metallothioneins secreted by *Phaeodactylum tricornutum* can detoxify copper ions. *P. tricornutum* releases metallothioneins, which combine with sulfide ions to create cadmium–metallothioneins complex. *Chlamydomonas reinhardtii* has a self-defense system involving detoxifying enzymes, hydrophilic antioxidants, and producing reactive oxygen species, to protect itself against cadmium and chromium toxicity described by [79].

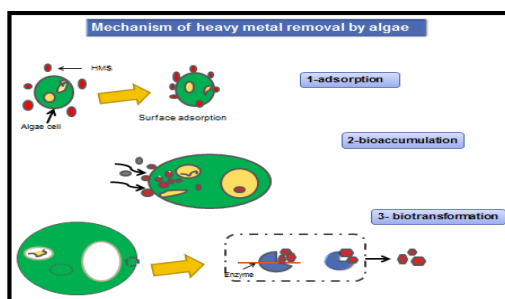


Figure3: Removal mechanisms of heavy metals by algae

3- Bioremediation of HMs by different algal species

The use of microalgae in biotechnology has grown in recent years, as it is used in several applications such as food, pharmaceutical, cosmetics, aquaculture, biofuel production, and others [80]. Microalgae are a kind of eukaryotic microbe that can only be found in watery environments and are phototrophic. It does this by removing carbon dioxide from the air via a process called photosynthesis and by controlling the rate at which its metabolism operates [81, 82]. A variety of microalgae can clean wastewater and reduce the amount of nutrients it contains [83].

Various of researchers have proposed that micro algae may be capable of detoxify HMs. Microalgae of the *Scenedesmus incrasatulus* genus were used in experiments conducted by [84] to extract chromium (VI), cadmium (II), and copper (II). Chromium (VI) was one of the toxic metals that have been considerably removed by *S. incrasatulus*. The findings indicate that *S. incrasatulus* taken away 25–78% of toxic metals. Similarly, [85] investigated removing zinc use of *Scenedesmus quadricauda* and *S. obliquus*. Experiment's results demonstrated that *S. obliquus* demonstrated a greater removing efficacy when compared to *S. quadricauda*.

When the a concentration of less than 0.5 mg¹⁻¹, [86] investigated ability of the micro-algae *Chaetoceros* sp., *Chlorella* sp., *Porphyridium* sp., and *Spirulina* sp., to remove HMs including Cd, Cu, and Pb. *Chlorella* sp. had the best elimination effectiveness of lead (90%) after 14 days of culture, followed by cadmium (62%) and copper (83%). On the other hand, *Porphyridium* sp. demonstrated the overall decrease of Cu (96%) and Cd (70%), while *Chaetoceros* and *Spirulina* sp. showed the least efficient elimination.

The bio sorption of Cd(II) and the kinetics of its elimination utilizing both live and non-living *C. vulgaris*. The findings demonstrated that these species has a high capacity for the adsorption of Cd both in its living cells (95.2%) and its non-living cells (96.8%)[87]. Research [88], the elimination of Cu and Ni by employing species of *Desmodesmus* and *C. vulgaris*. According to the findings, both types of microalgae could withstand the existence of copper and nickel for up to 12 days, and *Desmodesmus* sp. was able to eliminate more than 90% of the copper from sample of water.

The biosorption capability of *Scenedesmus* sp. for remove Cr (VI) from the solution. The findings indicated an accumulation of 92.89 percent Cr in the biomass of *Scenedesmus* sp. using a technique called Fourier transform infrared spectroscopy (FTIR), researchers were able to determine that the microalgae cell contained various kinds of functional sets. These sets involve positively charged amides, halides, phosphates, aldehydes, and carboxylic acids,. These sets all contribute to the biosorption process by being positively charged [89].

Using the resistant microalga *S. obliquus*, [90] investigated the process by which lead (II) is removed from the environment. According to the findings, *S. obliquus* ingested 85.5% of Pb(II) via biosorption, whereas only 14.5% of Pb(II) was accumulated through bioaccumulation.

The capability of several *Picochlorum* strains to remove HMs from a wide variety of wastewaters was investigated by [91]. These findings showed that various microalgae species have varied efficiencies for reducing HMs. The kinds of HMs present in the growth medium or wastewater also influence this efficiency. By using the desorption and adsorption approach, dead microalgal cells and products derived from microalgae may also eliminate HMs from the environment. Effects on algae by heavy metals and toxic mechanisms of it, show in (Figure 4).

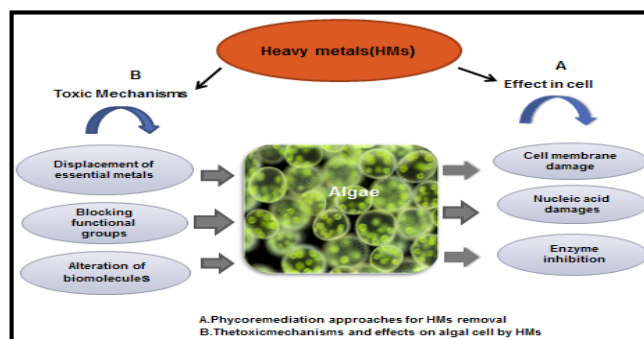


Figure4:Effects on algae by heavy metals and toxic mechanisms of it.

4- Abiotic factors influencing HM remediation by algae

4.1 pH

This factor is play important role in the component that determines adsorption. pH of the medium is an invariable agent that influences the availability of the metal-binding sets on algae. Despite the acidic environment, these sets can keep the surface negatively charged. On the other hand, a low pH (less than 2) was observed to reduce the amount of metal biosorption by microalgae. When there is a high amount of H⁺ ions, metal biosorption is reduced because this inhibits the metals' ability to attach to ligands on surface of the cell [92, 44]. According to the pKa of functional sets, the most important contributions to the biosorption of metals are phosphodiester, phosphate, sulfonate, and carboxyl sets. Due to the varying amounts of each functional set observed in various algal strains, various algae have varying capacities for the biosorption of metal ions [93].

In order to achieve optimum biosorption capacity and efficiency, optimizing the pH of the solution is essential. As a result, much work has been put into figuring out the ideal pH levels for increasing the amount of metal ions algae can remove [94]. *Padina australis* reached its maximum capacity for the biosorption of Cs⁺ at a pH of 4. [95]. The pH of the solution had important impact of Cu⁺² bio sorption. At acidic pH (2), there was reported to be a lower Cu⁺² biosorption. Between pH 3 and 4, the rise was

demonstrated to be the most significant [96]. The pH 5 was best for the bio sorption of Pb^{2+} by *Durvillaeaaprotatorum*[95].

When utilizing live algal cells, there is a possibility that the biosorption of certain metal ions, involving Pb^{2+} and Cu^{2+} , may increase because of that the photosynthetic activity of the algal cells will cause pH in the suspension to rise [97]. In this way, the acidity of the culture medium may be controlled by the infusion of carbon dioxide [44].

Researcher[98] found that the pH increased, further negative sites became obtainable for copper ions sorption, when high pH, can lead to increase the elimination of copper ions. They also found during the adsorption process, that the pH increased by about 0.1 to 1 unit from its initial value. On the other hand, no discernible link was found between the rise in pH and the consumption of copper ions. They supposed that the mass balance may have caused the shift in pH that the copper ion sorption had caused. In their research on *Sargassumfluitans*, [99] increased the pH from its starting value of 3.5 to its end value of 6.0 after adding *S. fluitans*. The results of their study were published in 1995. In addition, they discovered more sites were accessible for the sorption of metal ions when higher pH values, . As a consequence, the elimination efficiency rise with pH.

4.2 Temperature

Temperature impacts how well each metal ion is biosorbed by each kind of algae [100, 101]. Even though of the temp is the main determinant of the metal-ligand complex production constants, some research, asserted that the during of algal culture, increase of the temps might lead to an increase in metal ions biosorption without considering constant formation changes [102, 103].

Following factors could increase tendency of affective locations to absorb metal ions, decrease resistance to bio mass transmit in the dispersal layer due to a reduction diffusion boundary layer surrounding of biosorbent sets, rise the number of active groups involved in metal ion uptake, or alter complex formation constant with temp [104,105].

In living cells usually that the ideal temp range for active biological processes is small. At 20 and 45 degrees Celsius, respectively, the mass of *Chlorella Vulgaris* attained the greatest bio sorption of Ni^{2+} and Cd^{2+} [106]. The biosorption equilibrium of metal ions on non-living biomass of algae is influenced by temperature and the process's exothermic or endothermic character [107]. Compared to non-living algae, higher temp may have a bigger influence on the biosorption capacity of live algae because of biosorption and the role of enzymes in transported of ion [108]. Various algal race respond dissimilarly to absorption metal ions at various temps[109, 110, 111,112] According to [113], the dry biomass of *C. vulgaris* adsorbs more Ni^{2+} as the temp rises. On the other hand, the same researcher observed in a prior study [106] that a rise in temp (from 20 to 50 degrees centigrade) led to a decline the bio sorption of cadmium (II) biosorption capacity (from 85.3 to 51.2mg g⁻¹). Higher temps were claimed to result in less Cd^{2+} being absorbed by *Oedogonium* species by [114]; however other studies indicate that temp seems to have no impact on the sorption of metals [63]. [115]noted that while temp has a broad range of effects on metal biosorption, its effect is less significant than that of pH.

4.3 Ionic strength

Researcher found that the rate of elimination increase with decrease in ionic strength of the medium, which was true. However, playing of absence or presence of another ions in the medium and the growth rate, the nutrient content, and lighting was important roles, The number of functional sets remains the same regardless of the pH of the solution; however, the number sites that can accept metal ions decreases as the ionic strength of the solution increases. Consequently, removed ion is reduced when the ionic strength increases [116].

In the bioremediation by algae of HMs, a rise in the ionic strength of the wastewater is caused by presence of large quantities of monovalent cations (K^{+} and Na^{+}). In turn, this condition can cause a reduction in the metal biosorption capacity of the biomass [117].

The hypothesized that competition for the functional sets between metal ions and other ions had play a significant role in adsorption. Researcher assessed sorption of copper by calcium alginate, and they demonstrates that the elimination efficiency increases (from 80% to 95%)when the ionic strength reduces (from 0.5 to 0.005 mol^{l-1}), . On the other hand, high ionic strength decreases the extent of biosorption[118].

When studying the impact of ionic strength on the uptake of metals by algae, [119] found that there was increasing ion strong and pH with reduction in proton binding and an increase in Ni and Cu binding with increasing pH and reducing ionic strength. These findings were based on their observation that proton binding decreased as ionic strength increased. When there was a higher concentration of NO₃ in the culture medium, the absorption of Cd⁺²by *Aphanocapsa* was also higher [120].

The growth stage of the culture algae too affects the metal ions that are bioabsorbed, which could be a consequence of increased exposure of the metal binding sites or from the formation of additionally groups on the surface of cell while the culture is in the stationary or decline stage. Biosorption of Ni⁺²on was greater for cultures in the stationary and decline phases than for cultures in the exponential phase on the surface of *C. vulgaris*[121]. The growth circumstances may impact the metal ions biosorption properties of the biomass because the growth conditions influence the cell surface constitution, which is an important factor in metal ions biosorption [122],abiotic factors influencing HM remediation by algae, explain in (Figure 5).

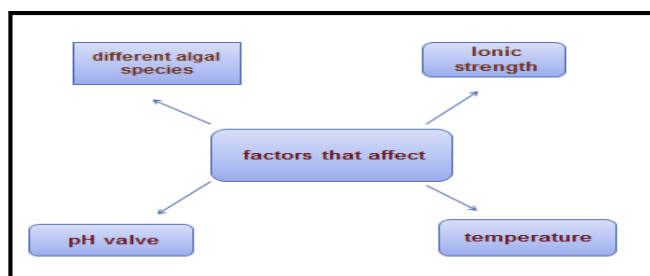


Figure5:Abiotic factors influencing HM remediation by algae.

CONCLUSION

Given the factors that have been discussed thus far. HMs pollution has appeared as one of the most significant challenges to the planet's ecology in recent years. HMs are non-biodegradable and may cause toxicity in humans, animals, and plants. Compared to more traditional methods for wastewater remediation, phytoremediation is the technique that has the least negative impact on the environment. Researchers can conclude that various species of algae possess multiple mechanisms for removing and detoxifying HMs. These mechanisms involve extracellular biosorption, intracellular bioaccumulation, and potential low-cost alternatives to physicochemical treatment methods. With these mechanisms' help, researchers could determine that various species of algae possessed multiple mechanisms. The effectiveness of algae in removing HMs is impacted by various factors, including pH, ionic strength, temp, and among others. Producing biomass which involves lipids and other metabolic material that could be utilized in the manufacture of biofuel, is one of the advantages that can be derived from coupling the cultivation of microalgae with the elimination of HMs from wastewater. To moreover contribute to the creation of a microalgae-based future, nevertheless, more research and approaches are needed to increase elimination rate and utilization of its biomass for application applications. These improvements are necessary to make. The investigation of the processes at play yields insights that may be used to increase processing selectivity and efficiency while also cutting costs. Because of bioremediation technology, we have been able to clean up the contaminated environment, and as a result, this might be utilized as a management tool.

Authors' Declaration

Conflicts of Interest:

The authors declare no conflict of interest.

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- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any Figures and images, that are not mine/ours, have been included with the necessary permission for re-publication, which is attached to the manuscript.

Ethical Clearance: The project was approved by the local ethical committee at University of Babylon.

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