Journal of Qassim University for Science
2025, *Vol 4* (Issue 1), pp. 193-221.
Received: 11 September 2023
Revised: 20 September 20233
Accepted: 24 September 2023
Published: 27 April 2025

JQUS

Biosorption of Heavy Metals by Algae: Recent Advances, Mechanisms, and Applications in Wastewater Treatment- A review

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Abstract

The global concern surrounding heavy metal contamination has intensified due to their elevated toxicities, non-biodegradable nature, the propensity to bioaccumulate within the human body and food chain, and their potential to induce cancer in humans. Various remediation techniques have been employed to isolate hazardous materials (HMs), with a focus on traditional methodologies. However, these methodologies often prove cost-prohibitive for large-scale projects, requiring meticulous oversight and continuous supervision. Additionally, their low efficiency compromises their effectiveness in removing hazardous materials. Multiple studies have provided compelling evidence supporting the potential of biosorption as a highly effective technique for eliminating heavy metals from aqueous solutions. Algae, due to their widespread presence in both seawater and freshwater environments, cost-effectiveness, reusability, and efficient metal sorption capabilities, are considered valuable biosorbents. This review presents a comprehensive analysis of recent research findings on various algae types' performance, applications, and chemistry for removing heavy metals from wastewater. The intricate mechanisms involved in the bioaccumulation and detoxification of heavy metals in algae are explored in this article. This review discussed the impact of various parameters, such as pH, temperature, initial metal concentration, biomass loading, and contact time, on the observed outcomes. Also, this article delves into the chemistry of metal biosorption by algal species, which possess numerous metal binding groups on their cell surfaces, including carboxylate, amine, imidazole, phosphate, sulfhydryl, sulfate, and hydroxyl groups. Algae, abundantly present in both marine and freshwater environments, have emerged as fundamental components in the recently developed metal biosorption process. This process has proven highly effective for detoxifying industrial effluents containing metals, showcasing its competitiveness in this domain.

Keywords: Heavy metals · Bioremediation, Algae, Wastewater treatment, Biosorption, Abiotic factors, Bioaccumulation.

Introduction

The expansion of metal and chemical usage in various industrial processes has generated significant volumes of aqueous effluents containing high concentrations of heavy metals. These heavy metals pose significant challenges in terms of environmentally responsible disposal. Additionally, mining, mineral processing, and extractive-metallurgical operations yield substantial quantities of liquid waste that contain hazardous substances. It is crucial to address the pressing need to reduce the levels of these harmful metals to environmentally acceptable and economically viable levels. This endeavor holds immense significance for sustainable practices and the preservation of our ecosystem [1-2]

The conventional methods of treating low-concentration heavy metals in wastewater, such as the ion exchange and precipitation methods, face several obstacles, including low efficiency, high cost, and the possibility of secondary pollution [3]. As a result, scholars have conducted thorough investigations into the application of cost-effective adsorbents such as clay, natural zeolites, chitosan, and other materials for the purpose of mitigating heavy metal contamination [4-9].

Furthermore, in the past few decades, a significant endeavor has been to discover new biosorbents to address heavy metal pollution [10,11]. The emergence of the biosorption idea can be attributed to investigating the effects of heavy metals on microorganisms in the context of fermentation processes. Various types of biomasses, regardless of their state (living or non-living) or moisture content (dry or wet), have been utilized in the process of removing heavy metals from wastewater [12].

The utilization of algae species for bioremediation, known as "phytoremediation", has emerged as a highly promising method for removing heavy metals from wastewater [12-14]. Phytoremediation offers numerous advantages over alternative bioremediation approaches. Firstly, it enables the use of algal biomass in wastewater with higher metal concentrations compared to membrane processes [16]. Secondly, algal biomass can be used without the need for synthesis, and it can be regenerated and reused in multiple adsorption/desorption cycles. Moreover, phytoremediation exhibits a high uptake capacity and efficiency in removing heavy metals [17]. Notably, this process avoids the generation of sludge or toxic chemicals. Additionally, the immobilization of macroalgal biomass is unnecessary, and phytoremediation can be applied in both discontinuous and continuous regimes. Furthermore, by utilizing dead biomass, there is no nutrient or oxygen supply requirement, making it suitable for both anaerobic and aerobic effluent treatment units. Another advantage is that algal biomass can be utilized year-round [18]. Lastly, phytoremediation is a cost-effective approach [19].

Given the significance of algae as a potentially effective method for removing heavy metals, this review aims to provide a comprehensive summary of current advancements in using algae for heavy metals remediation. The study focuses on the primary mechanisms of eliminating heavy metals: biosorption and bioaccumulation.

It offers a detailed discussion on the influence of various abiotic conditions on removing heavy metals and the subsequent modifications in algal biocomponents. Furthermore, the paper highlights the need for future research to develop sustainable wastewater treatment and biomass production technologies.

Phytoremediation

Phytoremediation, a field of study that has gained significant attention and recognition, involves harnessing the capabilities of algae to remove or reduce harmful substances, particularly heavy metals, from wastewater [20, 12]. Heavy metals pose a serious threat to both human health and the environment, making their removal from wastewater a critical concern for water quality and ecosystem well-being [21]. Phytoremediation offers a sustainable and cost-effective solution to address this challenge. Algae, as photosynthetic organisms, possess the unique ability to absorb and accumulate HMs through various mechanisms, including adsorption, ion exchange, and bioaccumulation [22]. These mechanisms enable algae to efficiently remove HMs from wastewater, leading to improved water quality. Moreover, algae can also transform HMs into less toxic forms through processes like biotransformation and biomineralization. The effectiveness of phytoremediation in removing HMs depends on factors such as the type and concentration of HMs, as well as the specific algae species employed [18].

In the realm of algae taxonomy, various classification systems have been developed based on morphological characteristics, such as cell wall structure, stored food materials, reproductive structures, and life history patterns. Algae can be categorized into seven primary groups, including *Rhodophyta, Chlorophyta, Charophyta, Chrysophyta, Euglenophyta, Pyrrhophyta, and Phaeophyta*, which are phyla within the kingdom *Protista* [19]. These classifications provide a framework for understanding the diversity of algae species and their potential applications in phytoremediation.

Trace elements play a vital role in the growth and development of algae, serving as micronutrients that are essential for their metabolic processes. For instance, algae require the presence of certain metal ions such as manganese (Mn^{2+}), nickel (Ni^{2+}), copper (Cu^{2+}), molybdenum (Mo^{2+}), iron (Fe^{2+}), zinc (Zn^{2+}), and others in trace amounts [19]. However, the excessive presence of heavy metal ions can have detrimental effects on algal populations and overall ecosystem health [19].

To further explore the topic of heavy metal removal, in-depth studies have been conducted on specific ions, including tin (Sn^{2+}), gold (Au^{3+}), cadmium (Cd^{2+}), lead (Pb^{2+}), strontium (Sr^{2+}), titanium (Ti^{3+}), and mercury (Hg^{2+}) [20, 12]. These investigations delve into the behaviors, interactions, and potential remediation techniques associated with these heavy metal ions. The understanding of their impact on algae and the development of effective strategies for their removal is crucial for advancing the field of phytoremediation.

Biosorption: A Sustainable Approach for Metal Removal

The biosorption process is a phenomenon that involves the use of biological materials, such as microorganisms or plant biomass, to remove or recover pollutants from aqueous solutions. The concept of biosorption was initially explored in the mid-20th century, and since then, significant efforts have been made to develop cost-effective biomaterials for wastewater treatment. Various biomasses have been found to selectively eliminate hazardous pollutants from water at low concentrations and under diverse conditions, attracting attention from multiple scientific disciplines. Advancements in understanding the complex mechanisms of biosorption have been achieved through the establishment of quantitative techniques, such as equilibrium and kinetics studies, and the identification of influential factors that affect its effectiveness and speed [23].

Adsorption refers to the process in which ions and molecules adhere to the surface of a solid material through physicochemical processes [24]. The physical connection between metals and biosorbents is influenced by electrostatic and Van der Waals forces, while the chemical aspect involves processes like ion exchange, proton shift, complexation, and metal chelation [25]. Biosorption is a rapid and reversible phenomenon where ions from aqueous solutions bind to functional groups on the surface of biomasses, independent of cellular metabolism [26].

Biosorption offers an environmentally friendly and cost-effective alternative for metal recovery from diluted solutions. It utilizes sustainable and economically viable sorbents derived from various sources, including bacterial cultures, algae, fungi, agro-industrial waste, and aquaculture waste. The efficiency of biosorption is influenced by metal properties such as concentration, molecular weight, ionic radius, and oxidation state. Similarly, the characteristics of the biosorbent, such as surface area, porosity, and functional groups, play a significant role in the biosorption process [26].

The biosorption method exhibits distinct features that impact its practicality and effectiveness, including cost considerations, biosorbent storage requirements, metal selectivity, and biosorbent reusability. These features collectively contribute to the potential and applicability of biosorption as a viable solution for pollutant removal in wastewater treatment.

Preserving Biosorbents: Exploiting the Advantages of Stabilized Biomass in Biosorption

An advantageous characteristic of employing stabilized (non-living) biomass in biosorption is its remarkable ability to effectively preserve biosorbents over extended durations. Previous studies have reported the absence of any detrimental effects caused by heavy metals. Furthermore, stabilized biomass demonstrates excellent performance across a wide range of pH and temperature conditions, and its potential for chemical regeneration enables its reuse in adsorption-desorption cycles [27-29] (Table 1).

Primary investigations into biosorbents have predominantly focused on microorganisms, including bacteria, cyanobacteria, fungi, and macroalgae, along with their corresponding extracts. While plants and other biomasses offer insights into biosorption to a lesser extent, all types of biomasses share a common characteristic: the presence of a cell wall comprised of biopolymers. However, the specific composition of these biopolymer chains varies among different organisms. For instance, bacteria possess cell walls composed of peptidoglycan, while algal cell walls contain fucoidan and alginate. Each biopolymer contains chemical residues that harbor functional groups capable of interacting with metals, facilitating their physical retention or chemical complexation, ultimately leading to biosorption (Figure 1).

The Potential of Algae as Biosorbents

Algae have emerged as a focal point in the realm of research and development of innovative biosorbent materials. Their exceptional sorption capabilities and abundant availability in virtually unlimited quantities have contributed to their prominence. A comprehensive statistical analysis conducted on biosorption studies revealed that algae have become the preferred biosorbent material, surpassing other biomass forms by a significant margin of 15.3%. Furthermore, algae have exhibited an impressive utilization rate of 84.6%, outperforming fungi and bacteria in terms of application efficacy. Among the various types of algae, brown algae have garnered the highest level of interest, outshining red and green algae. In a study conducted by Brinza et al. [30], it was discovered that brown algae possess a greater absorption capacity compared to their red and green counterparts.

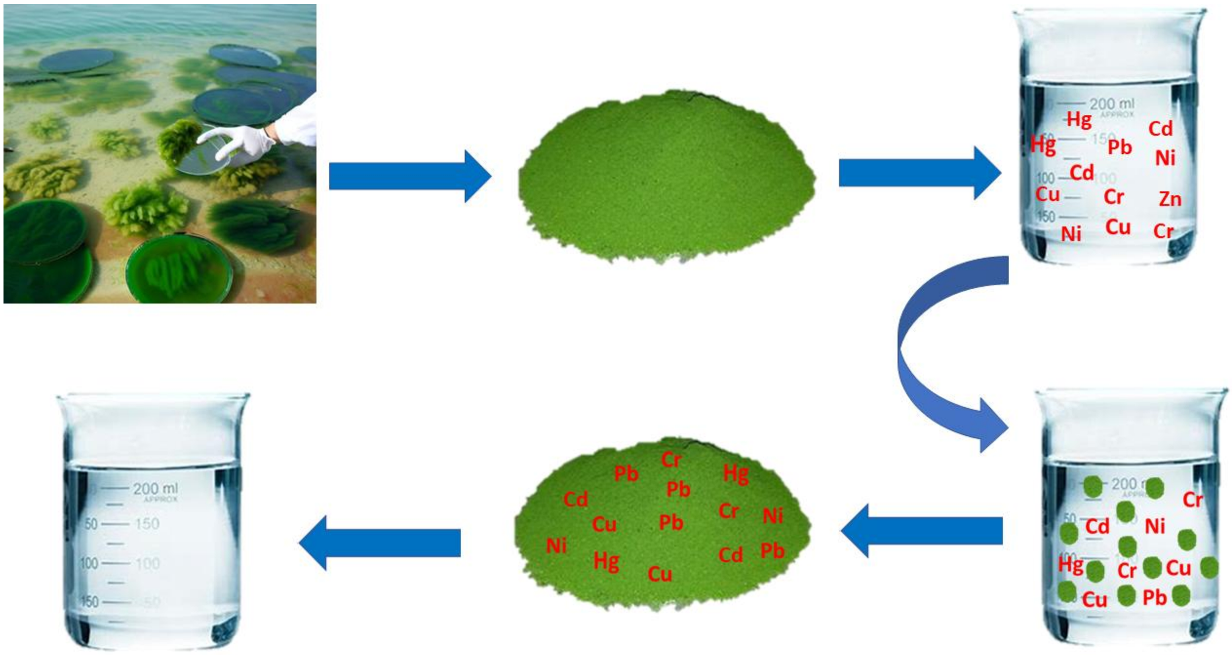

Figure 1. Schematic representation elucidating biosorption processes for heavy metal removal using algae.

Biosorbents possess the remarkable property of metal sequestration, enabling them to reduce the concentration of heavy metal ions in a solution from ppm to ppb levels. The behavior of biosorbents towards metallic ions is contingent upon the chemical composition of the microbial cells comprising them [31]. Seaweeds derived from marine environments serve as cost-effective reservoirs of biomass. Davis et al. [26]

conducted a study focusing on marine algae, particularly brown algae, to explore their potential for metal removal. Extensive efforts have been dedicated to enhancing the biosorption process, encompassing areas such as immobilization techniques and optimization of reuse. In the field of biosorption, various types of algae have been utilized and examined to determine their effectiveness in the process. The algal cell is encompassed by a complex, thin, and resilient cell wall, which plays a pivotal role in metal biosorption. The composition of the cell wall, especially the cell surface and spatial organization, largely influences the process of metal binding by the biomass.

Overall, algae offer immense potential as biosorbents owing to their exceptional sorption capabilities, abundant availability, and diverse species variations. Continued exploration and optimization of algae-based biosorption processes hold promise for addressing metal pollution challenges effectively and sustainably.

The Potential of Immobilized Algal Biosorbents

Immobilized algal biosorbents have emerged as valuable materials for the adsorption of various substances. The utilization of immobilization technology plays a crucial role in facilitating the practical implementation of biosorption, particularly when employing non-living biomass. Microbial cells are unsuitable for column packing due to their low density and size, leading to bed plugging and significant pressure drops. Various matrices suitable for biomass immobilization include alginate, polyacrylamide, polyvinyl alcohol, polysulfone, silica gel, cellulose, and glutaraldehyde [12].

In the context of biosorption applications in industries, it is essential to employ an appropriate immobilization strategy to develop commercial biosorbents that maintain the metal adsorption capability of microbial biomass throughout continuous treatment processes. Immobilizing biomass onto solid structures has the potential to provide a biosorbent material with the necessary dimensions, mechanical integrity, stiffness, and porosity required for practical applications. These immobilized materials can be utilized in a manner similar to ion exchange resins and activated carbons, specifically through adsorption-desorption cycles.

The Biosorption Process Utilizing Non-Living Algal Biomass

A study conducted by Eneida Sala et al. [32] demonstrated that the non-living species *Sargassum sp*. has the capability to absorb various metal ions, including cadmium, chromium, and copper.

Batch investigations have indicated that *Sargassum* seaweed effectively biosorbs chromium, with the biosorption capability significantly influenced by the pH of the solution. The size of the biosorbent did not have a significant impact on both the biosorption capacity and rate. Another investigation conducted by Davis et al. [26] examined cadmium and copper absorption in six distinct *Sargassum* species. The maximum biosorptive capabilities were found to be 0.9 m.mol/g for *Sargassum sp.,* 0.89 for *S. filipendula,* 0.93 for *S. vulgare,* and 0.8 for *S. fluitans*. Additionally, *Ascophyllum nodosum* demonstrated a maximum Cu uptake of 0.037 m.mol/g, as indicated in Table 1.

The Intricate Process of Heavy Metal Bioaccumulation and Detoxification in Algae

Bioaccumulation is a complex process in which heavy metal ions traverse live cell membranes through various mechanisms, such as active and passive transport channels, leading to their accumulation within cells (Figure 2). The build-up of heavy metals within the cell has been found to hinder photosynthesis activity, reducing algal growth. Moreover, this accumulation causes an irreversible increase in plasma membrane permeability, leading to the loss of cell solutes. Additionally, it disrupts membrane integrity by compromising protein structure and displacing essential metal ions, resulting in enzyme inhibition. Certain algae have exhibited abnormal morphological development and loss of flagella as a consequence. Algae have employed intracellular and extracellular metal-binding strategies, such as ion exchanges, chelation, physical adsorption, and complexation, to mitigate the toxicity of heavy metals [33]. These processes' efficacy lies in transforming harmful metals into non-toxic forms [34].

Table 1. A comparative analysis of metal biosorption capacities across different algal species.

Type of algae	Metal Examined	Capacity of Biosorption		References
		m mol/g	mg/g	
Candida albicans biomass	Pb (II)		833	[27]
Sargassum sp.	Cd (II)	0.9		[26]
Sargassum sp.	Cr (II)		68.94	[32]
S. filipendula	Cd (II)	0.89		[26]
S. vulgarae	Cd (II)	0.93		[26]
Callithamnion corymbosum	Cu (II)		24.25	[35]
Callithamnion corymbosum	Co (II)		9.89	[35]
Callithamnion corymbosum	Zn (II)		19.12	[35]
Ulva fasciata sp.	Cu (II)		26.88	[36]
Ulva fasciata sp.	Zn (II)		13.50	[36]
Codium vermilara sp	Cu (II)		16.90	[37]
Codium vermilara sp	Zn (II)		23.80	[37]
Padina sanctae crucis sp.	Cu (II)		13.99	[38]
Padina sanctae crucis sp.	Co (II)		13.73	[38]
Durvillaea potatorum	Cs			[39]
Durvillaea potatorum	Pb(II)			[39]
Durvillaea potatorum	Cu (II)	1.30		[40]
Ascophyllum nodosum	Pb(II)	1.31		[41]
Ascophyllum nodosum	Pb(II)	0.86		[37]
Padina pavonia	Pb(II)	1.04		[42]

Padina sp.	Cu (II)	1.14		[43]
Sargassum sp.	Cu (II)	1.13		[44]
Ascophyllum nodosum	Cu (II)	0.91		[37]
Fucus spiralis	Zn (II)	0.81		[37]
Macrocystis pyrifera	Zn (II)	0.91		[45]
Sargassum vulgare	Ni (II)	0.09		[41]
Sargassum sp.	Ni (II)	0.61		[43]
Sargassum filipendula	Ni (II)	1.07		[46]
Sargassum sp	Cr (VI)	0.60		[47]
Sargassum fluitans.	UO2(II)	1.59		[48]
Fucus spiralis	Pb (II)		204.1	[37]
Scenedesmus quadricauda	Cu (II)		75.6	[49]
Spirulina platensi in alginate gel	Cd (II)		70.92	[50]
Spirulina platensis in silica gel	Cd (II)		36.63	[50]

Algae employ various mechanisms to detoxify metal, including binding to specific intracellular organelles or transportation to specific cellular components like polyphosphate bodies/vacuoles. Metal detoxification can also occur through the expulsion of metals into the surrounding solution via efflux pumps. Furthermore, algae have the capacity to synthesize phytochelatins or class III metallothioneins, contributing to their metal detoxification processes [51]. The detoxification process can potentially reduce the toxicity of heavy metal ions on cellular organisms by causing their precipitation in the forms of carbonate, phosphate, or sulfide [52].

Fucus vesiculosus, a macroalga, exhibited a remarkable ability to accumulate significant levels of heavy metals from saltwater contaminated with these substances. Specifically, it was able to remove 65, 95, and 76% of Pb, Hg, and Cd, respectively. The bioconcentration factors for Pb, Hg, and Cd ranged from 600 to 2300, indicating that all of these metals were deposited in the biomass after being extracted from the solution [53].

Influential Factors in the Process of Metal Accumulation

The process of metal uptake by inanimate biomass is subject to several physical and chemical factors, which impact biosorption through diverse adsorption mechanisms. This section delves into the study of how different operating conditions affect the extent of metal uptake.

pH of the medium

The Role of pH: As mentioned earlier, the biosorption process resembles an ion exchange mechanism, making the pH of the aqueous solution a critical factor in metal uptake. The pH level influences the metal-binding sites on the cell surface and the chemistry of metal ions in the solution. Numerous researchers have investigated the effects of aqueous solution pH on metal uptake [33, 39, 40].

A common trend observed across various metals and biomass is limited metal uptake at extremely low pH levels, typically within the pH range of 1 to 2. The absorption of metal ions shows an upward trend as the pH is raised within the range of pH 3 to 5, eventually reaching an optimal pH value where metal uptake is maximized. However, as the pH exceeds the optimal range, there is a decline in metal uptake.

At extremely low pH levels characterized by a high concentration of protons, competition arises between metal cations and protons for available binding sites on the cell walls. This competition leads to a decrease in metal uptake by the cells. Yu and Kaewsarn [40] suggest that the observed decrease in metal uptake when pH is reduced from 4 to 2 is likely due to an elevated concentration of hydronium ions (H_3O^+) at lower pH levels. At pH 2, the absorption of metal ions is reduced as they compete with H_3O+ ions for binding to complexation sites (Table 2). Zhou and Kiff

[54] propose that under low pH conditions, cell-wall ligands have a close association with H_3O^+ ions, restricting access of metal ions to the ligands due to repulsive forces.

Table 2. A comparative examination of the pH levels in the medium of biosorption across different algae species.

Type of algae	Metal Examined	pH of biosorption medium	References
Sargassum sp.	Cd (II)	6.8	[26]
Sargassum sp.	Cr (II)	4	[32]
S. vulgarae	Cd (II)	6.8	[26]
Callithamnion corymbosum	Cu (II)	4.4	[35]
Callithamnion corymbosum	Zn (II)	4.4	[35]
Ulva fasciata sp.	Cu (II)	5.0	[36]
Ulva fasciata sp.	Zn (II)	5.0	[36]
Codium vermilara sp	Cu (II)	5.0	[37]
Codium vermilara sp	Zn (II)	5.0	[37]
Padina sanctae crucis sp.	Cu (II)	6.0	[38]
Padina sanctae crucis sp.	Co (II)	6.0	[38]
Durvillaea potatorum	Cs	4	[39]
Durvillae potatorum	Pb(II)	5	[39]
Durvillaea potatorum	Cu (II)	2	[40]
Ascophyllum nodosum	Pb(II)	3.5	[41]
Ascophyllum nodosum	Pb(II)	3	[37]
Padina pavonia	Pb(II)	4.5	[42]
Padina sp.	Cu (II)	5	[43]
Macro Algae	Cu (II)	5.4	[55]
Neochloris oleoabundans	Pb(II)	6	[56]
Neochloris oleoabundans	Hg(II)	5	[56]
Neochloris oleoabundans	Zn (II)	7	[56]
Neochloris oleoabundans	Cd (II)	4	[56]
Neochloris oleoabundans	Cu (II)	7	[56]
Ulva flexuosa	Cd (II)	4	[57]
Ulva flexuosa	Co(II)	4	[57]
Ulva flexuosa	Zn (II)	4	[57]

As pH levels increase, there is greater exposure of ligands with a negative charge, resulting in an increased attraction towards positively charged metal ions [58]. Yu and Kaewsarn [40] found that the capacity of biomass to uptake metals was lowest when the pH of the biomass reached its isoelectric point. Above the isoelectric point, the ligands in the biomass acquire a net negative charge, enhancing their interaction with metals. However, it was also observed that metal binding occurred below the isoelectric pH, even with ligands carrying a positive charge. This indicates that not all binding sites on the biomass are solely influenced by electrostatic forces.

A study by Luef et al. [59] noted that biomass treated with NaOH exhibited heightened metal absorption. This treatment effectively removed a significant portion of the cell wall material containing carboxyl and phosphate groups. These findings suggest that metal binding is not solely governed by electrostatic interactions but involves the participation of other functional groups.

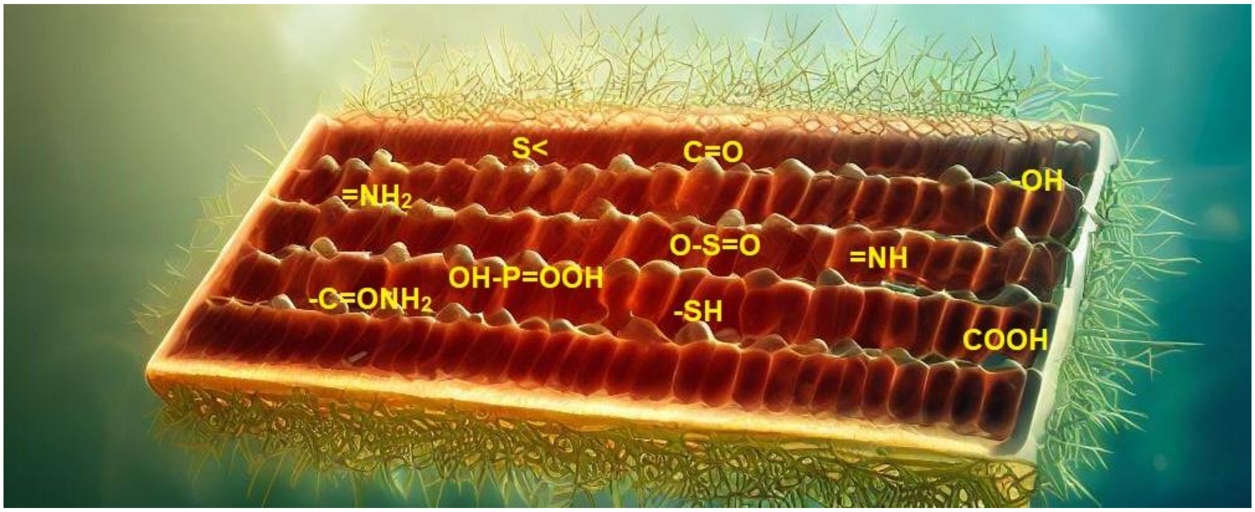

Figure 2. The key functional groups on the algal cell wall surface involved in heavy metal biosorption.

The influence of increasing pH values on metal chemistry in the solution is significant in determining the extent of metal absorption. The decrease in metal absorption as pH is elevated above the optimal range (pH 5 to 7) can be attributed to decreased solubility and the formation of metal precipitates [39].

Ionic strength

Ionic strength is a measurement of ion concentration within a solution. It is determined by calculating the sum of all ions' concentrations. The impact of ionic strength on metal interaction with algal biomass is influenced by the competitive attachment of heavy metals and sodium ions (Na^+) through electrostatic forces. When the ionic strength is high, the negative charges on the algal biomass are effectively neutralized. However, when the ionic strength decreases, electrostatic forces increase protons' concentration within the particles, surpassing the proton concentration in the surrounding solution [60, 61].

A pKa value of 3.0 was assigned to all algae, assuming that the volume of cation binding is directly proportional to the number of binding sites. The binding constants of Cu^{2+} followed the sequence: *Sargassum* > *Petalonia* > *Colpomenia* > *Ulva*. The inherent binding constant of Cu^{2+} was found to be 30-90 times higher than that of Ni^{2+} [46].

Covalent binding was more significant for Cu^{2+} compared to Ni^{2+}, as Ni^{2+} was primarily bound through electrostatic attraction. The occurrence of covalent metal binding in *Ulva* was limited, possibly due to alginate's absence in green algae. This absence results in insufficient carboxyl groups appropriately spaced for metal ions to bridge between two binding sites. Brown algae, as stated by Davis et al. [26], are more suitable for biosorption applications compared to green algae due to their higher metal binding capacity and affinity.

The influence of the initial metal concentration

The influence of the initial metal concentration on the effectiveness of metal removal using macroalgae was investigated by Rangabhashiyam and Ahmad et al. [62, 63], revealing that macroalgae exhibited higher efficacy when the inflow concentrations of metal were low. At low metal concentrations, a high proportion of sorptive surface area to accessible metal ions results in the binding and removal of nearly all metal ions in solution. As the concentration of metal ions increases, there is a corresponding decrease in the percentage of metal uptake. Therefore, the authors propose that the biosorption process shows enhanced effectiveness in treating dilute solutions when a significant removal percentage is required over extended periods. According to the findings of Younis and Aly-Eldeen [1], the highest percentage of metal uptake was observed at low initial concentrations. Conversely, the specific uptake per gram of biomass increased as the inflow concentration was raised. Younis et al., [58] found a positive correlation between the initial metal uptake rate and the starting concentration. However, the largest percentage of metal removal was observed at low concentrations. For instance, *Pistia stratiotes* has demonstrated efficient accumulation and detoxification of cadmium at low concentrations, particularly at 10 mg/L. This capability is attributed to various mechanisms, including biosorption and intracellular binding. Within this specific range, the bioremoval process exhibits a notable level of efficacy [1]. Conversely, it has been observed that elevated metal concentrations, such as 100 mg/L, can adversely affect the efficiency of the bioremoval process facilitated by *Swietenia mahagoni*. Specifically, the absorption capacity of Cr(VI) is hindered, leading to a decrease in the overall removal efficiency [62].

The influence of biomass

The influence of biomass loading on metal uptake is a significant factor that can affect the removal of metals from a solution. Previous studies have consistently shown that, at a specific equilibrium concentration, biomass adsorption by metal ions is more pronounced at lower cell densities than at higher cell densities [64].

Younis [58] proposed that the dependency of metal adsorption on biomass concentration could be influenced by electrostatic interactions between cells. They suggested that an increased distance between cells would result in the adsorption of a larger number of cations.

Mohamed et al. [65] found that a decrease in biomass content in the suspension at a specific metal concentration led to an increase in the metal/biosorbent ratio. Consequently, this resulted in a higher metal uptake per unit of biosorbent as long as the biosorbent was not saturated. Pons and Fuste [66] hypothesized that a high biomass concentration could lead to a "screening" phenomenon, where the densely packed outer layer of cells acts as a protective barrier, shielding the binding sites from metal exposure. As a result, the absorption of a specific metal, which refers to the amount of metal removed per unit biomass, is reduced at elevated biomass densities. The presence of a substantial amount of biomass, indicated by high biomass densities, leads to a greater extraction of metal from the solution. Therefore, in order to optimize the percentage of metal removed from the solution, it is necessary to have higher biomass densities.

The impact of contact time

The duration of contact strongly influences the biosorption of heavy metal ions. Previous studies have highlighted the specific kinetics of HM ions biosorption on algae cell surfaces, showing variations among different algal strains [9]. As Chang [67] and Gupta et al. [68] discussed, biosorption can be divided into two distinct stages. In the case of algal biomass, metal ions passively adsorb onto cell membranes, resulting in a rapid occurrence of biosorption within the initial minute. In the presence of live algae, active biosorption occurs as the algal cells gradually absorb the heavy metal ions. Studies conducted by Sooksawat et al. [69] and Vogel et al. [70] demonstrated that non-living C. vulgaris biomass achieved over 90% absorption of uranium (U) within the initial 5-minute period. Similarly, microalgae *Chlamydomunas reinhardtii* exhibited rapid adsorption of Hg(II), Cd(II), and Pb(II) free ions, reaching biosorption equilibrium within 60 minutes [71]. These findings highlight that algae adsorption of heavy metal ions is a passive phenomenon that occurs relatively quickly, even in the absence of live algal cells. However, the biosorption capacity of living algae is significantly influenced by the duration of contact time.

Metal Biosorption Chemistry

The elimination of metal ions using inert, lifeless biomass relies on the phenomenon of metal sorption, which occurs due to the strong attraction between the metal ions and the biomass. Figure 3 illustrates the intricate characteristics of this mechanism.

The adsorption capability of marine algae can be attributed to their fundamental biological composition [72]. The primary factor responsible for heavy metal sequestration is the unique characteristics of cell wall materials, namely alginate and fucoidan. Brown algae, red algae, and many green algae commonly have cell walls composed of a fibrillar skeleton and an amorphous embedding matrix. The fibrillar skeleton is predominantly composed of cellulose, while the embedding matrix consists of alginic acid or alginate (alginic salts) and sulfated polysaccharide (fucoidan) for brown algae and sulfated galactan for red algae.

Brown and green algae possess critical functional groups, including carboxyl, hydroxyl, sulfate, phosphate, and amine groups, which have been found to significantly influence metal bonding processes [68, 43] (Figure 2). The carboxyl group, with a pKa value of approximately 5.0, is particularly important for metal binding. Additionally, the sulfonic acid groups of fucoidan also contribute to metal binding but to a lesser extent [26].

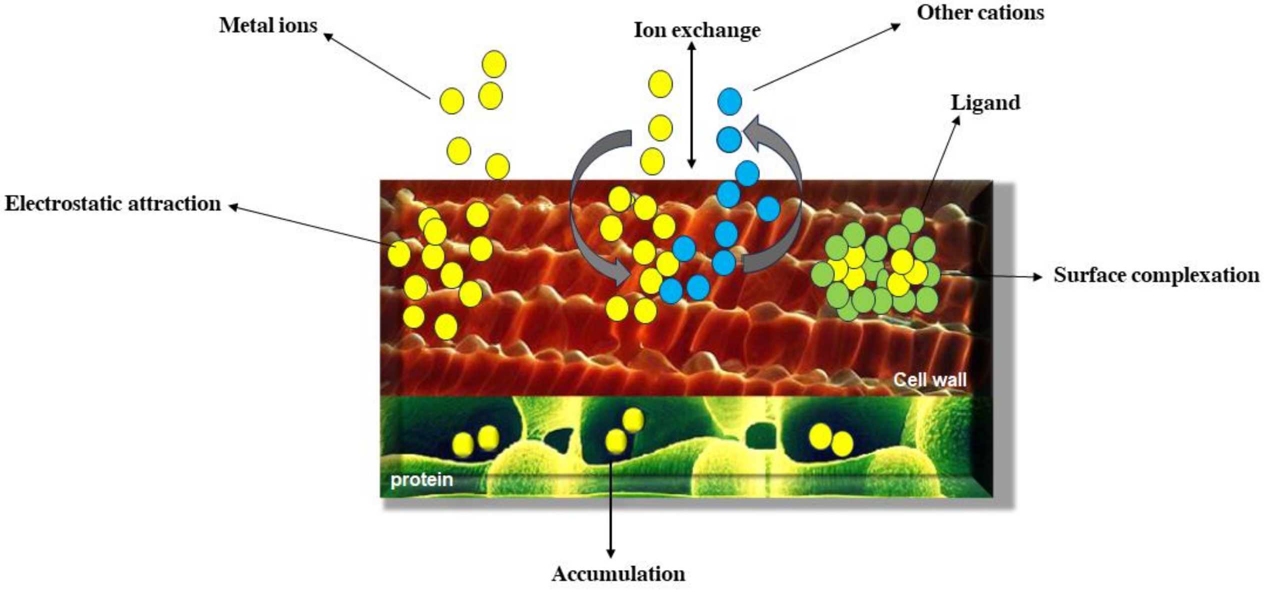

Figure 3. Adsorption pathway of heavy metals on algal cell walls

The interaction between different functional groups and heavy metals during biosorption has been investigated using spectroscopic techniques such as FT-IR and XPS [73]. Heavy metal ions become attached to functional groups on the surface of cells through processes such as ion exchange, complexation, chelation, and microprecipitation [74, 75]. Existing research indicates that the major functional groups found in algal cell walls, specifically alginate and fucoidan, are the primary contributors to the biosorption of heavy metal ions [76, 77].

Ion exchange has been observed to play a significant role in marine-derived biosorbents (Figure 3). The process involves the exchange of heavy metals with light metals, primarily involving Ca^{2+} and Mg2+, as monovalent Na+ and K+ do not result in significant cross-linkage [78].

Alginates derived from brown algae exhibit a greater affinity for divalent cations such as Pb^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+}. These alginates are found within the cell wall and intercellular material. Coordination or complexation processes are also observed in the binding of heavy metals by alginate and sulfated polysaccharides like fucoidan [26]. Stereochemical effects influence the binding of metal ions to alginate or fucoidan, with larger ions having a greater propensity to occupy a binding site that accommodates two spatially separated functional groups. The affinity sequence observed is as follows: $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Ni^{2+} > Ca^{2+} > Mg^{2+}$.

According to Romera et al. [37], sulfated polysaccharides, specifically Galatians present in red algae, play a primary role in the formation of metal ion complexes. X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy (FTIR) have been extensively used to elucidate the interaction mechanisms between functional groups in biosorbents and metal ions.

The adsorption mechanism of metals onto algae involves a range of physical and chemical interactions. Biosorption, through complexation, ion exchange, and electrostatic interactions, plays a significant role in metal attachment to algal cell surfaces. Surface adsorption, driven by van der Waals forces and hydrogen bonding, is also involved. Extracellular polymeric substances (EPS) released by algae enhance metal adsorption capacity. Additionally, intracellular accumulation occurs as metals permeate algal cell membranes and associate with intracellular components. It is important to note that the adsorption mechanism may vary depending on the specific metal and algae species. Understanding these mechanisms is essential for developing effective bioremediation systems utilizing algae for metal removal (Figure 3).

Conclusion

The comprehensive examination of the application of marine algae in the elimination of heavy metals from aqueous solutions has received considerable attention in recent years. The evaluation and comparison of the biosorption capabilities of unprocessed algae, as well as modified algae and their derivatives, have been conducted. The process in question is intricately linked to the biochemical composition of algae, namely their cell walls, as well as the chemical properties of the surrounding water. The elimination of heavy metals can be accomplished through the utilization of biosorption mechanisms. The efficacy of heavy metal elimination by algae is impacted by various crucial factors, such as pH, temperature, ionic strength, duration of contact, and the existence of counter ions. Based on the findings discussed in this comprehensive review, it is evident that algal species offer significant advantages as biosorbents, making them a promising eco-friendly alternative to conventional ion exchange processes. Consequently, this study provides guidance for future research endeavors focused on the advancement of sustainable technologies that utilize algal bioremediation to effectively treat wastewater containing high concentrations of heavy metals. This approach holds great potential for addressing environmental concerns and achieving efficient and effective remediation of heavy metal-contaminated wastewater.

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