Algal Biomass Valorization for the Removal of Heavy Metal Ions

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Abstract Pollution generated by wastewater containing inorganic pollutants, such as heavy metals, has always been considered a real problem for our planet. Therefore, the removal of these micropollutants from polluted water is a valuable intervention to preserve human health and the environment. Many conventional methods are used today to treat wastewater, such as membrane filtration, chemical precipitation, ion exchange, and adsorption by activated carbon, but the operating cost they generate has restricted their use. To overcome this limitation, scientists have focused for always on the application of marine resources to clean up the environment. The adsorption of heavy metals by biosorbents obtained from algae has been widely studied for wastewater treatment, as the exploitation of this biomass has the advantage of being a low cost, renewable and abundant biological raw material, and its use as a biosorbent is also a great alternative to activated carbon. The sorption capacity of the vegetable adsorbent is depending on chemical constitution of their cell wall and the presence of macromolecules with various functional groups that interact with metal ions. We review in this chapter, (1) the challenges associated with heavy metals, such as water pollution, hazardous effects, and their removal techniques including biosorption based on algae biopolymers, such as alginate and carrageenan, (2) the main chemical and structural compounds of macroalgae responsible for the metal ions removal, (3) current knowledge on the potential of macroalgae regarding their pharmacological applications and possible biosorbents prepared from them for the removal of metal ions from aqueous solutions.

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1 Introduction

Heavy metal pollution is among the phenomena that received throughout the world an increasing attention, it has become a serious global environmental problem and a major concern. The interest in these pollutants is mainly linked to the harmful effects they have on human health, as well as on other organisms living in the aquatic environment, because of their bioaccumulation, toxicity, and non-biodegradability properties, these pollution problems are due to the environmental disorder caused by the fast growth of industrial activities [102].

The adverse effects of these molecules on humans depend on some factors such as dosage, emission rate, and exposure period. Moreover, the toxicity level of some heavy metals for humans was found to follow the order Co < Al < Cr < Pb < Ni < Zn < Cu < Cd < Hg [81]. Among these toxic micropollutants, Hg, Cd, and Pb have received more attention for the last decades, because of their toxicity and their effects on the environment and the living organisms [157]. Few of these inorganic pollutants such as zinc and iron are needed for human defense, plants, and other living beings, but although the importance occupied by them, they can pose health hazards if their concentrations exceed allowable limits. As an example, the excess of zinc has main symptoms for human, such as nausea, dizziness, electrolyte imbalance, and muscle stiffness [5, 53].

If some metals have demonstrated their main function in human body, there are some that are toxic even at low concentration as the case of cadmium, which is a non-biodegradable element in nature, and up to day it has not been proven to have any physiological function in human body [54]. Another point is that a chronic exposure to Pb(II) even to low concentration decreases the intelligence capacity of children [81]. As a result of the critical effects of heavy metals, concerned environmental agencies, such as the World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA) set safe limits for heavy metals in recycled, in drinking water, and in wastewater [108]. The safe limits of heavy metals in wastewater samples as well as in drinking water according to the WHO guidelines are listed in Table 8.1.

For many decades, various conventional technologies were employed to remove metals from aqueous effluents, such as chemical precipitation (hydroxide and sulfide precipitation), ion exchange, membrane filtration, coagulation/flocculation, flotation, and electrochemical treatment [9]. Each of these processes has its disadvantages [48]. These limitations have led researchers to find other alternative methods such as adsorption, especially which focus on the use of abundant and less expensive biomaterials. The widely used adsorbent around the world is activated carbons, but the increased cost of these materials and some complexities involved in their synthesis limited their use. Therefore, low-cost adsorbents must be developed to

Table 8.1 World Health Organization guidelines for safe limits of heavy metals

Sample	Metal ions	Safe limits (ppm)	References
Wastewater	Pb(II)	0.01	Ayeni [14]
	Ni(II)	0.02	Ayeni [14]
	Cr(III)	0.05	Ayeni [14]
	Hg(II)	0.001	Onuegbu et al. [113]
	Cd(II)	0.003	Ayeni [14]
Drinking water	As(V)	0.01	Sayato [137]
	Cd(II)	0.003	Sayato [137]
	Pb(II)	0.01	Sayato [137]
	Hg(II)	0.006	Sayato [137]
	Ni(II)	0.07	Sayato [137]
	Cr(III)	0.05	Sayato [137]
	Zn(II)	5	King et al. [80]

replace the current expensive adsorption method of removing heavy metals from solution. Hence, searching for an alternative of activated carbon from abundant and inexpensive sources is of concern [48].

A number of researches have been carried out on biosorption using both the micro and macroalgae biomass [19, 68, 69, 121]. The marine macroalgae have demonstrated their ability toward the removal of inorganic pollutants including heavy metal ions [93]. The good removal capacity of these resources is due to the surface structure, which contains active functional groups involved in the biosorption process [69]. Biosorption by dried seaweeds has been intensively studied in recent years as an economical treatment for the removal or recovery of metals from industrial effluents [59, 70, 140]. Applying dried seaweeds in the adsorption of these ions present several advantages such as wide availability, low cost, high metal sorption capacity, and reasonably regular quality [12]. This process implies the use of dried macroalgae or their derivatives to adsorb the metal ions with the ligands or functional groups located on the external surface of them. The passive elimination of some of these toxic pollutants as the case of Cd^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cr^{3+}, and Hg^{2+} by inexpensive biomaterials requires that the adsorbent has certain adsorbent properties such as high selectivity and high metal uptake [33].

2 Metal Pollution and Health Effects

Heavy metals are the most toxic pollutants, and the resulting pollution is considered a worldwide environmental problem. The discharge of industrial wastewater without prior treatment or with insufficient treatment leads to dangerous effects on the one hand, on marine organisms living in aquatic environment and on human health as the main consumer in the food chain of marine resources, on the other hand, on the state of the wastewater treatment plant and that of the sanitation network.

Heavy metals are defined as metallic elements that have a relatively high density compared to water, they are characterized by a high atomic weight and a density approximately five times higher than that of water [151]. They present in many industrial effluents generated by numerous anthropogenic activities, such as plating facilities, mining operations, and tanneries, as well as, they are continuously released into the biosphere by volcanoes due to natural weathering of rocks [17, 157]. Heavy metals, such as cadmium, arsenic, lead, and copper, are among the common inorganic pollutants of serious concern in wastewater treatment, they are particularly characterized by their high toxicity, and even in trace amounts, they can cause serious disturbance to aquatic organisms and health problems for humans [142]. Several studies have focused on the exploitation of marine resources as a source of alternative applications more suited to current environmental challenges including heavy metal pollution [86, 95, 96]. The following paragraphs will highlight some of the effects of heavy metals, which have taken a large part in the recently published studies regarding the biosorption of inorganic pollutants by marine macroalgae.

Cadmium, which is known under the symbol Cd, it is a chemical element from group IIB of the transition metals of Mendeleev's periodic table, with atomic number 48 and atomic mass of about 112.4 g/mol [112]. This metal is used in various domains such as accumulators or alkaline batteries, pigments for paints or plastics and in electrolytic process by deposit or by cadmium plating on metals or to reduce melting points. Cadmium is a known cumulative toxic substance whose disposal half-life is about 20–40 years; it is stored primarily in the liver and kidneys after entering the body [11]. This metal poses serious risks to human health, and it has not been shown to have any physiological function in human body [54].

Arsenic is another heavy metal, which occupies a considerable place in the published data concerning the field of biosorption due to its toxicity and danger. Arsenic is a chemical element with atomic number 33 designated by the symbol As, and it is generally considered a metalloid. Arsenic occurs naturally in its two forms of oxyanions, namely, arsenite As(III) and arsenate As(V) [138], as well as it occurs in the –3, 0, + 3, and + 5 oxidation states [143]. Numerous studies have been conducted as an attempt to solve the problem of arsenic pollution and to find the most efficient technology to remove its species from drinking water and industrial wastewater [28, 61, 138]. The main source of pollution caused by arsenic in the environment is the smelting of ores, such as those of gold, silver, and copper. As a result, arsenic from these sources is distributed in the air, water, soil and finds its way into human body through direct inhalation or contamination of food and consumer products.

Lead, known as Pb, it is a chemical element with atomic number 82. It is a natural constituent of the earth's crust, and it is commonly found in soils, plants, and water in trace amounts. This metal usually exists in ores, which also contain other metals such as copper and zinc, which are extracted as a co-product of these metals. Lead is a toxic heavy metal that can reach human body by inhalation and ingestion from various sources, such as contaminated air, water, soil, and food. Lead has become the most common toxic metal in the world due to human actions, and today, this metal is widely used in different sectors including, building construction, fusible alloys, bullets, and lead-acid batteries [26].

Copper is another kind of inorganic pollutants that have been extensively studied by researchers regarding the field of bio-absorption [29, 97]. Copper is a chemical element with atomic number 29 known as Cu. It is a member of the family of metals included in the periodic table of the elements. Copper is an essential nutrient for humans, animals, and plants, but it can be hazardous to human health at high exposures. This metal can exist in the form of free cationic Cu^{2+} under acidic conditions, and trace amounts of $[Cu(OH)]^+$ and water-soluble $Cu(OH)_2$ under neutral and basic conditions [72].

3 Technologies of Wastewater Treatment

Currently, various technologies are applied for the removal of heavy metals from industrial wastewater in large conventional treatment plants. The following section highlights the most commonly used methods for this purpose including chemical precipitation, ion exchange, membrane filtration, electrochemical, flotation, and adsorption. For a brief comparison, the advantages and disadvantages of each treatment method are listed in Table 8.2.

3.1 Chemical Precipitation

Due to its simplicity, chemical precipitation is considered among the most widely used conventional processes to remove heavy metals from inorganic effluents [84]. This process is based on a mechanism in which an insoluble metal is produced by the reaction of the metals dissolved in solution and the precipitant [56]. In this process, the positively charged molecules and those negatively charged (anions) are combined. As well as, the dissolved metal precipitation is compelled by increasing the soluble anion concentration [61]. Very fine particles are then generated at the end of this process. Therefore, chemical precipitants, coagulants, and flocculation processes are used to increase their size and in order to remove them as sludge [56].

3.2 Ion Exchange

Ion exchange is another example of the technologies used to treat polluted effluents. This technique is based on the attraction of soluble ions from the liquid to the solid phase. In addition, the resins used in this method, which are hydrophobic solid

Table 8.2 Comparison of applied technologies to heavy metal ions removal from wastewaters

Process	Advantages	Disadvantages	References
Chemical Precipitation	• Low capital cost • Simple operation	• High operating cost • High cost of disposal of produced sludge	Wang et al. [159]
Ion exchange	• Metal-selective, • eLimited-pH tolerance • High regeneration	• High-initial-capital • High-maintenance cost	Gao et al. [51]
Membrane filtration	• High efficiency • Appropriate for a variety of wastewater compositions	• Membrane fouling • Secondary pollution • Short lifespan of membranes • High operation cost	Hube et al. [67]
Electrochemical treatment	• Cost effective • Effective at ambient temperature • Electrode materials with long operating life	• Blockage of electrodeposition due to the metal hydroxide precipitation • Wasted energy and unstable process	Chaplin [25] Liu et al. [95, 96] Tran et al. [153]
Adsorption	• High efficiency • Capacity to remove metals • Less chemical consumption	• High operating cost, • The efficiency decrease with the presence of other metals	Da'na [31]

substances, can retain positively or negatively charged ions from an electrolyte solution and at the same time release other ions of a similar charge in the solution in an equivalent quantity [56]. The process of ion exchange should not be confused with solvent extraction, the difference being that the first indicates the separation of solid from liquid, and the second means the separation of liquid from liquid. Furthermore, this technique is considered a valuable technique for recovering minerals from the mining process and mining tailings using chelating resins [71].

3.3 Membrane Filtration

This technology makes it possible to obtain purified water by passing it through special filter membranes, which physically retain the impurities present in water. Various types of membrane filtration such as ultrafiltration, nanofiltration, and reverse osmosis can be used to treat wastewater containing heavy metals. In general, these methods of separation have been of growing interest both for the treatment of drinking water and wastewater. Ultrafiltration and nanofiltration are effective for the removal of all classes of pollutants. Whereas, microfiltration is not much use for the treatment of these effluents because of its large pore size [124]. Reverse osmosis is another membrane separation technique that uses pressure to allow the solution to pass through a membrane that retains the solute on one side and allows the solvent to move to the other side [56].

3.4 Electrochemical Treatment

The electrochemical method is a technology that allows to eliminate heavy metals from wastewater. It consists in making these micropollutants precipitate in a weakly acidic or neutralized catholyte in the form of hydroxides [56]. The main reagent used during this treatment is the electron, which is a clean reagent. Thus, there is no need to add any additional reagent [125]. The electrochemical wastewater treatment involves electroplating, electrocoagulation, electroflotation, and electrooxidation [56]. This technology is chosen to treat these effluents because it offers ideal tools for addressing environmental problems.

3.5 Adsorption

Adsorption process is defined as a surface phenomenon by which one or more than one adsorbate are fixed to the adsorbent surface and form binding through physical or chemical bonds. This process is recognized as the most promising and efficient fundamental approach in the wastewater treatment processes [44]. One of the main adsorbents employed to treat waste effluents is the activated carbon, because it contains a developed surface area with large porous. For commercial carbons, usually, their surface area is ranging from 500 to 1500 m^2/g and sometimes even up to 3000 m^2/g. Coal, lignite, bone charcoal, and wood are among the main raw materials extensively employed in the preparation of these adsorbents [134].

Despite the advantages of the previously listed physicochemical methods in the treatment of polluted effluents, they can sometimes load the natural environment with organic pollutants more toxic than the original ones. As well as, these methods are known to be very expensive and require sophisticated equipment. Another point is that activated carbon is recognized as the most powerful adsorbent, its industrial application is prevented by the high cost associated with its production [10]. These limitations, led researchers and industrialists to focus on finding other more efficient and less expensive methods, including biosorption based on the use of biomaterials prepared from cheap and abundant resources.

Biosorption is defined as a process in which substances of aqueous phase are removed by passive bonds created between the substrate and the dead biomass or derived materials [2]. Many data in the literature have been used to describe the biosorption process the following terms; sorption, bio-adsorption, and removal regarding organic and inorganic pollutants [15, 27, 45, 49, 139]. This interfacial phenomenon, should not be confused with the accumulation or bioaccumulation that indicates the absorption. As explained above, the biosorption involves a surface phenomenon where metal ions are attached to the dried algae, while bioaccumulation requires the metabolic activity of a living organism to sequester these pollutants [2].

Recently, research has intensified on the mechanisms of biosorption by which biomass is used to remove or to recover precious metals from processing solutions [2]. Adsorption is still considered as a phenomenon in which a complex and poorly understood mechanism is involved. It depends on the type of organism whether is alive or not, the type of microorganism and the elemental species [106]. This mechanism explains how the metal ion is binding to the biomass. Commonly, these mechanisms are classified as either physical, chemical, or electrostatic adsorption [118]. Ion exchange has been shown to be an important concept in biosorption, as it can explain many observations made in heavy metal uptake experiments [33]. Ion exchange, complexation, and coordination are of the main mechanisms behind the uptake of heavy metals by macroalgae [136]. In addition to the previously mentioned mechanisms, adsorption, precipitation, and covalent binding may also be involved, but the most likely is ion exchange [90].

The functional groups of algae cell walls play vital roles in biosorption. Carboxylic and sulfate groups are known to be the main metal bending functional ionic groups in the cell wall of algae [90]. Carboxylate groups of alginate have been identified as the main binding site for metals [98]. Thus, there is a scientific and practical interest in identifying the active sites of the bio polymeric structures involved in the sorption. For this purpose, the determination of different functional groups that may be involved in biosorption process is mandatory. The Fourier transform infrared spectroscopy analysis (FTIR) provides information desired on these functional groups and the molecular bonds of biosorbent are investigated [8]. This spectroscopy over the last decades has proven and accepted to be a powerful tool for studying biological samples [37]. FTIR analysis coupled with potentiometric titration was used to identify and quantify surface functional groups of algae. In this regard, some functional groups were identified to be the predominant in the surface of the three classes of marine algae, namely, carboxyl, hydroxyl, amino, and sulfate groups [136]. These functional groups work as binding sites for metal and are located at the surface of the cell wall as polysaccharides, proteins and lipids.

Among the previously discussed groups, the hydroxyl groups especially present in all polysaccharides can be negatively charged, which contributes to the adsorption of metals at a high level [46]. The possible functional groups that participate in heavy metals biosorption are, hydroxyl, carboxyl, amino, ester sulfhydryl, carbonyl, and phosphate groups, they are found in alcohols and carbohydrates, fatty acids, proteins and organic acids, proteins and nucleic acids, lipids, cysteine, aldehydes and polysaccharides, deoxyribonucleic acid and tissue plasminogen activator, respectively [9]. Phaeophyceae cell wall has been characterized by its composition rich in chemical functional groups, such as hydroxyl, carboxylic phenolic acid, and amine involved in the biosorption process that is induced by the selective binding and interaction created between the metals or any other pollutants and the biosorbent [108]. To study various aspects involved in the biosorption of metal ions, the potential of biosorption and some other parameters must be calculated based on the equations.

$$q_t = \frac{V(\mathrm{C}_i - C_t)}{m} \tag{8.1}$$

$$\%Removal = 100\frac{C_i - C_f}{C_i} \tag{8.2}$$

where q_t is the biosorption capacity usually expressed in mg of metal per g of biosorbent, subscript t indicates adsorption capacity at a given time (t). C_i, C_t, and C_f indicate the initial concentration, the concentration at given time, and at equilibrium time (ppm), respectively. V is the volume of metal ion solution (L), and m shows the biosorbent mass (g).

4 Marine Algae

Macro and microalgae are a diverse group of photosynthetic and aquatic living organisms that are lacking advanced structures in their cell alignment and morphology [147]. They range from unicellular to multicellular. Algae can grow both in fresh and marine water. As well as, and compare to agricultural plants, they require only less space [147]. In addition, they can be harvested throughout the year compared with other crops that are usually harvested once or twice a year [107].

Algae are able to produce oxygen, consume carbon dioxide, act as the base of the aquatic food chain, remove nutrients and pollutants from water, and to stabilize sediments [89]. Moreover, these photoautotrophic prokaryotic and eukaryotic organisms are capable to assimilate nitrogen and phosphorus from the medium in the biomass during their growth, and the biomass generated can then be converted into various bioproducts following the apposite process [95, 96].

Algae are classified into two main types depending on their size: (i) microalgae, which are a diverse group of photosynthetic microscopic organisms. Chemical energy is produced by microalgae by converting the solar energy based on photosynthesis like terrestrial plants. These microorganisms are suitable candidates to produce oil. There are several methods to retrieve this oil, but the choice of which one will be used is madding according to the properties of the algae [21], (ii) macroalgae, which concern us much in this chapter, also known as seaweeds, as their name indicates macroalgae are a group of aquatic organisms that are visible to the naked eye. It should be noted that there is another type of classification, which suggests that algae can be classified into three categories according to their growth habits, namely, microscopic algae, filamentous mat-forming algae, and the Chara/Nitella group, and each of the previously mentioned groups causes its own unique problems to water system [89].

5 Macroalgae

5.1 Classification and Use of Macroalgae

Based on their pigmentation, botanists divided marine macroalgae into three main categories, which include (i) red algae (rhodophyceae), which include 390 genera with 1810 intraspecific species or taxa, (ii) brown algae (phaeophyceae), that include 96 genera with 596 infraspecific species or taxa, and finally, (iii) green algae (chlorophyceae), which comprises 77 genera with 585 infraspecific species or taxa [141]. The pigment responsible for the red color of rhodophyta is phycobilins, and the brown color of phaeophyta comes from fucoxanthin, while; many pigments (e.g., chlorophyll a and b, carotenes and xanthophylls) are behind the green color of chlorophyta, the main characteristics of marine macroalgae are summarized in Table 8.3 [114]. Moreover, the chemical structures of some chlorophyll behind the color of these species are shown in Fig. 8.1. Seaweeds are often used as a source of food and as a promising sustainable alternative to conventional terrestrial animal feed resources, for their mineral content or the functional properties of their polysaccharides. The high content of some components in the macroalgae, such as alginate and carrageenan, hinders the use of these seaweeds in the feed of monogastric animals, because the passage of these polysaccharides in their digestive tract is often without any digestion [114].

Marine macroalgae are well recognized in Asia, in Japan for example, seaweed is an important part of many daily meals, they represent up to 10% of the total nutritional intake of some cities as Kombu, Nori, Wakame, and Hijiki [115]. Moreover, the current human consumption in terms of green, brown and red algae is 5%, 66.5%, and 33%, respectively, this is high in Asia mainly in Japan, China, and Korea [85].

According to FAO estimates of the year 2014, 38% of the 23.8 million algae recorded in the 2012 world harvest were consumed by people in recognized forms as seaweeds, such as kelp, nori, or lava not counting the consumption of agar, alginates, and carrageenans extracted from these algae and used as thickening food additives [161]. This marine biomass is not limited to human consumption and feed production,

8.3 Main characteristics of macroalgae

Common name	Divisions	Pigments	Type of cell wall	Main components of cell wall
Brown algae	Phaephycophyta	Chl a, Chl c, Phycoxanthin	Double	Cellulose, alginic acid
Red algae	Rhodopheacophyta	Chl a, Chl d, Beta-carotene, Zeaxanthin	Double	Cellulose
Green algae	Chloropheacophyta	Chl a, Chl b, Beta-carotene	Single	Cellulose

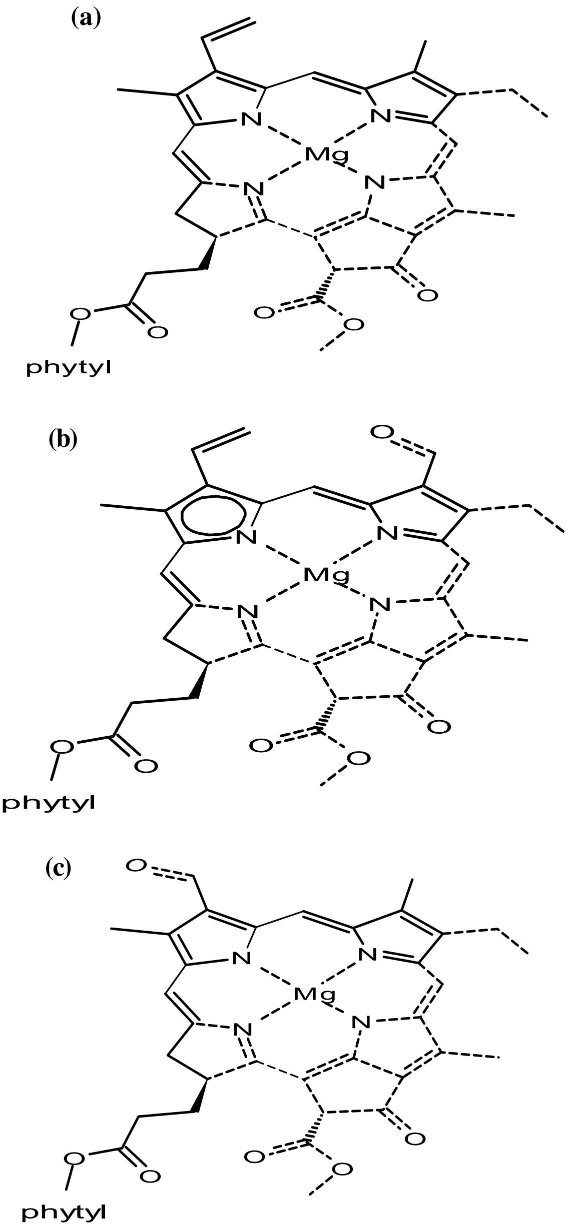


Fig. 8.1 Structures of chlorophylls: **a** Chlorophyll a, **b** Chlorophyll b, **c** Chlorophyll d

but it can also be exploited as water purifier because it recycles polluted water from fish waste in aquaculture [85].

5.2 Chemical and Structural Composition of Macroalgae

Algae are considered a promising material to be used as a biosorbent to clean wastewater from inorganic and organic pollutants, such as heavy metals and industrial dyes, this is mainly due to their rich biochemical composition [108]. Besides the pigmentation, they present various chemical and structural compositions [39]. This composition is generally constituted of three main components that are proteins, lipids, and carbohydrates [148]. Some of these constituents especially carbohydrates, proteins, and polysaccharides are commonly used to identify the type of macroalgae.

Lipids, the composition of macroalgae is characterized by different classes of fats, such as polyunsaturated fatty acids (PUFAs), triglycerides (TAGs), unsaturated acids and sterols, and the content of each class is depending on the season in which the algae were harvested. Nelson et al. [111] investigated three macroalgae species, namely, *Egregia menziesii* (phaeophyta), *Chondracanthus canaliculatus* (rhodophyta), and *Ulva lobata* (chlorophyta) to examine their total lipids content as well as their lipid classes in terms of diacylglyceryl ethers, wax esters, free fatty acid, sterols and polar lipid, this content was monitored for 4 months, namely December, March, July, and October 1997–98 that represent winter, spring, summer, and autumn, respectively. It was found that the dominant class of lipids in all algal samples was polar lipids, this result normally means that most lipids are structurally bound in membranes. Regarding the total lipid content, *U. lobata* showed the highest lipid content recorded in the spring (29 mg/g), while *C. canaliculatus* has been characterized with a low lipid content ranging from 1, 7 to 3.1 dry mass (Table 8.4).

In the same context, three macroalgae were investigated, namely, the chlorophyta *Ulva lactuca Linnaeus*, *Jania rubens*, and the rhodophyta *Pterocladia capillacea* to evaluate their major components content including lipid, all samples were harvested in April, August, and October 2010, corresponding to spring, summer, and autumn, respectively [75]. *Ulva lactuca* has shown to contain more lipids (4.09 ± 0.2%) than *Jania rubens* and *Pterocladia capillacea.* The green algae *Ulva lactuca* seems to be among the most lipid-rich macroalgae, with a content of 3–4% of the algal dry weight (Table 8.4). The lipid class that makes seaweeds more appropriate for biodiesel applications is TAGs [149]. The red alga *Gracilaria verrucosa* was studied in order to evaluate its total lipid content and the proportion of lipid fractions during the different stages of development. Male gametophytes were shown to have the highest amount of TAGs that are contained in the lowest total lipid content measured compared with all stages of development studied [77].

Proteins, regarding the protein content of marine algae, vary depending on the species type. In general, algae show such a marked variation in their constituents due to the effect of certain factors, such as the season of the year, the habitat, and the depth in which they grow [22]. Protein-rich algae are used in industry as food

Table 8.4 Chemical composition of macroalgae (% dry weight)

Macroalgae	Lipids	Proteins	Carbohydrates	References
U. lactuca	3–4	17–20	42–46	Khairy and El-Shafay [75]
J. rubens	1–2	10–13	34–42	Khairy and El-Shafay [75]
P. capillacea	2–3	17–24	48–51	Khairy and El-Shafay [75]
E. intestinalis	0.22	9.67	44.71	Pramanick et al. [122]
U. lactuca	0.38	8.77	37.87	Pramanick et al. [122]
C. repens	0.16	7.1	31.45	Pramanick et al. [122]
G. cervicornis	0.43	22.96	63.12	Marinho-Soriano et al. [101]
S. vulgare	0.45	15.76	67.80	Marinho-Soriano et al. [101]
U. lactuca	1.64	7.06	14.60	Wong and Cheung [162]
H. japonica	1.42	19.00	4.28	Wong and Cheung [162]
H. charoides	1.48	18.4	7.02	Wong and Cheung [162]
U. armoricana	2.6	–	–	Kendel et al. [74]
S. chordalis	3.0	–	–	Kendel et al. [74]

additives, as well as a high protein content has been reported in some red algae [43]. The biochemical composition of some macroalgae showed that the red alga *Gracilaria Cervicornis* has the highest protein content 22.96% compared with other species harvested during the same seasons of the year (Table 8.4). Even if, some published data gave a value of 32% for the protein content of the green alga *Ulva lactuca*, but this was judged to be a high seasonal value [43]. It was reported that the red macroalga *Porphyra yezoensis* can have up to 47% protein expressed on a dry weight basis [50]. Moreover, this content was found to be higher even than that of legumes recognized for their high-protein content such as soybeans [43].

The extraction of proteins from seaweeds is difficult due to the complex polysaccharide of the cell wall and extracellular matrix, which is somewhat species dependent [114]. The protein fraction containing in the macroalgae may be calculated based on the determination of elemental nitrogen using the nitrogen–protein conversion factor of 6.25 according to AOAC method [91].

Carbohydrates and Polysaccharides, each algal division has its typical carbohydrates. For example, the carbohydrates in brown algae species consist mainly of alginates, laminaran (β-1.3-glucan), cellulose, fucoidan, and mannitol [82]. The cell wall of marine algae and other components of the cell matrix consist mainly of structural polysaccharides existing in the form of heteropolysaccharide complex [116]. A large amount of these polysaccharides is in their sulfated form, which includes the three main phycocolloids, namely brown algae alginates, red algae carrageenan, and agar, and these biopolymers are in high demand in the hydrocolloid industry [116]. These polysaccharides have a significant importance both technologically and economically. Furthermore, Agar, alginate, and carrageenan are the three high-value algal hydrocolloids, they are used as gelling and thickening agents in different food, pharmaceutical, and biotechnology applications [129].

Pramanick et al. [122] investigated three macroalgae, namely, *Enteromorpha intestinalis*, *Ulva Lactuca,* and *Catenella Repens* to compare their biochemical components. Their proximate composition was found to follow the order carbohydrate > protein > fat > astaxanthin (Table 8.4). The estimation of carbohydrate fraction is achieved by the phenol–sulfuric acid method developed by Dubois et al. [35].

Earlier studies have indicated the effect of some environmental factors, namely, light, temperature, salinity, and nitrogen availability on the growth and biochemical compounds of marine macroalgae [36, 63, 76, 117, 128, 152]. Similarly, some researches have displayed that the growth conditions, such as phosphate limitation, nitrogen deprivation, and high salinity would affect more specifically lipid content [126, 127, 132]. For example, the protein and carbohydrate contents of *Ulva lactuca* are strongly affected by temperature and incubation time with an optimum at 30 °C for 24 h of incubation [120]. The nutritional content of marine algae is also strongly dependent on geographic locations and seasonal variations. Table 8.4 presents the average seasonal composition of some macroalgae species reported in the literature.

6 Macroalgae Potential and Applications

6.1 Pharmacological Potential

The search for metabolites with pharmacological potential in different divisions of macroalgae has developed considerably and has become one of the researcher’s concerns worldwide. In addition, a continuous and great effort is being made by academic and corporate institutions to identify biological activities in extracts of this biomass with the desired potential [7, 16, 47] (Al-Malki 2020). The interest in seaweeds may be explained by different advantages that they present compared with other biomasses. The present section brings into light the macroalagae extracts as a source of bioproducts exhibiting biological activities, such as antibacterial, antitumoral, and antileishmanial activity for possible pharmacological applications.

Ainane [8] investigated two marine algae namely, *Cystoseira tamariscifolia* and *Bifurcaria bifurcata*, to isolate extracts in order to evaluate their pharmacological potential according to a range of biological activities, namely, antibacterial, antileishmanian, antitumoral, and cytotoxicity activity. The technique used during the extraction process is the Soxhlet, it allows a continuous solid–liquid extraction using cycles of vaporization—condensation of the solvent. Four organic extracts were obtained from successive Soxhlet extraction with solvents of increased polarity, namely, hexane, ether, chloroform, and methanol. Each obtained extract was tested with the following activities; antibacterial activity tested using four bacterial strains, *Escherichia coli*, *Enterobacter cloacae*, *Klebsiella pneumoni,* and *Staphylococcus aureus*, while the antitumor activity tested based on the interaction with the DNA of the calf thymus, the antileishmanial activity tested toward *Leishmaniain fantum*, and finally the cytotoxicity activity tested toward the larvae of a saltwater shrimp: Artemia Salina. All the extracts from *C. tamariscifolia* and *B. bifurcata* showed an interesting inhibition zone against the three strains *E. cloacae*, *K. pneumoni*, and *E. colis*, except the hexanic extracts, which do not show remarkable activity against the latter strain.

Salari et al. [133] examined the antibacterial activity of nanoparticles synthesized through the bio-reduction of silver ions into the desired silver nanoparticles (SNPs) using the green alga Spirogyra varians. The bacterial strains used to evaluate the SNPs activity are *Bacillus cereus, Staphylococcus aureus, Escherichia coli, Listeria monocytogenes, Pseudomonas aeruginosa,* and *Klebsiella*. The reported results have shown a remarkable antibacterial effect against *Klebsilla, P. aeruginosa,* and *B. cereus*, and this activity was greater even than that of standard antibiotics.

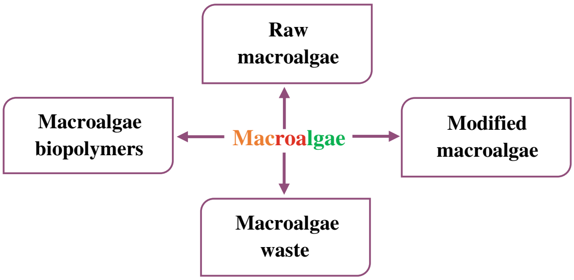
The inhibition concentrations relative to the different extracts of *Bifurcaria bifurcata* where 50% of cells are inhibited (IC50) have a significant activity compared with those of *Cystoseira tamariscifolia*, as well as IC50 of the hexanic extracts of *Bifurcaria bifurcata* are much better than other extracts of the same species with a remarkable value of 46.83 ppm [8].

Freile-Pelegrin et al. [47] used 27 species of macroalgae that belong to the three algal categories, namely, red, brown, and green algae to test their antileishmanial activity in vitro against Leishmania mexicana (L. Mexicana). The extracts from *Dictyota caribaea*, *Turbinariat urbinata,* and *Lobophora variegata* (phaeophyta) and from *Laurencia microcladia* (rhodoyta) showed a promising activity against L. Mexicana with a lethal concentration of 50% (LC50) values ranging from 10.9 to 49.9 ppm.

Whereas, some researchers were unable to demonstrate antitumoral activity in some of the macroalgae extracts [8], a group of researchers have proved that this biomass is a source of various bioproducts with biomedical properties that are capable to treat various types of diseases, such as cancer and inflammatory bowel diseases [135]. The extracts of *Sphaerococcus corono pifolius*, namely n hexane, dichloromethane, and acetone/methanol, exhibit the inhibition effect of diseases, namely, the proliferation of cancer cells of the cervix, breast cancer cells, and pancreatic cancer cells by inducing apoptosis [135]. Moreover, ethyl acetate fraction of *Tubunaria conoides* was tested and showed high anticancer activity through exhibiting synergistic effects over the respective standard compounds [119].

Abourriche et al. [4] proved that methylene chloride (CH_2Cl_2) fraction of *Cystoseira tamariscifolia* has a cytotoxicity activity against *Artemia salina*, with a lethal dose 50 (LD50) of 41.7 ppm. Furthermore, the extracts of *Bifurcaria bifurcata* were found to be toxic more than those of *Cystoseira tamariscifolia* toward the larvae of Artemiasalina [8]. To know the cytotoxic potential of macroalgae, the results of their LD50 must be compared with those of the active products used as a reference, such as digitalin 151 ppm, podophyllotoxin 2.4 ppm, and bebeerine chloride 22.5 ppm [103].

Fig. 8.2 Possible forms of dried macroalgae for biosorbent preparation



6.2 Macroalgae Biosorbents for Heavy Metal Removal

Numerous studies have been conducted looking at the use of marine macroalgae as low-cost biosorbent materials for the removal of heavy metals from wastewater [8, 30, 33, 99, 133, 164]. While, some researchers have focused on the use of another type of biomasses such as plants to remove these pollutants from aqueous solutions. In this context, Chiban et al. [28] investigated the Moroccan plant *Withania frutescens* to remove arsenic (V) from aqueous solution. The authors have shown the effectiveness of using this plant as biosorbent with a removal rate of arsenic reaching 73%, obtained by controlling some physicochemical parameters. In the present section, the possible biosorbents obtained from marine macroalgae are reviewed considering their application in the removal of heavy metal ions. According to our humble summary of the data reviewed in this study, the various potential sources of sorbents prepared from dried biomass can be grouped into four main categories as shown in Fig. 8.2.

6.2.1 Raw Macroalgae

Apart from marine algae, there are many other forms of raw biomass, which are currently used either to enhance the removal rate of adsorbents or as a source to prepare adsorbent materials for further use in removing organic and inorganic pollutants from aqueous solution, such as clays, plants, fungi, bacteria, and yeasts [15, 23, 110, 123, 165]. The complexity of the raw biomass structure indicates that there are many ways involved in the removal of pollutants, but these remain poorly understood [2].

Biosorbents can be derived from dried raw macroalgae without undergoing any significant pretreatment that is normally applied to increase their adsorption capacity. In this case, macroalgae are exposed only to a preliminary preparation during which undesirable objects are removed from the recovered samples after their collection. This preparation step remained similar in all data covered by this study with slight differences. The use of dried algae in their raw form seems to be advantageous as they are a natural and renewable material, and if they are directly applied in the biosorption process as a biosorbent, which indicates no costs are involved other than transport and simple approaches for their preparation [136]. It should also be noted that even after a simple preparation, such as washing and drying, these adsorbents have important chemical properties that contribute to the removal of many pollutants from the aqueous solution. Usually, during the preparation step, samples go through four main steps: washing with distilled water in order to remove any adhering debris, drying in the sun or in an oven, grinding/crushing, sieving to select particles of the desired size, and finally the obtained samples are kept for later use. The exploitation of algal biomass in its raw form for biosorbent preparation has proven its effectiveness in the removal of heavy metals, and this can be seen through the various publications regarding the potential of this non-activated biomass. Kumar et al. [86] studied the adsorption potential of adsorbent prepared from *Ulva fasciata* without prior pretreatment for the retention of Zn ions. This alga has demonstrated a good zinc biosorption capacity with a maximum adsorption of 13.5 mg/g, which highlights the potential of this alga in the treatment of wastewater.

6.2.2 Modified Macroalgae

Numerous attempts have been carried out regarding the use of efficient techniques to give new functionalities to bioserbent's surface, as well as to understand the fundamental aspects of the biosorption mechanism [5, 34, 98]. Research and development of new biosorption materials involve the use of seaweeds, especially those popularly named brown algae, because of their high sorption capacity, which is similar to that of commercial ion exchange resins, and their availability in almost unlimited quantities in the ocean [98]. This biomass can be exploited in its original form with a sample preliminary preparation (washing and drying) as mentioned above, as it can be used after passing through important chemical and sometimes physical treatments to increase its adsorption capacity toward metal ions dissolved in an aqueous solution. On the whole, surface modification methods can be categorized into two main types: chemical and physical modification.

(a) Chemical Modifications

Marine algae are chemically treated to enhance their sorption ability and reinforce their applications. The biosorbent prepared from this marine biomass can be modified by various functional groups depending on the nature of the metal ion to adsorb. These modifications can be made by a cross-linking reaction using epichlorohydrin to harden the cell wall structure [79], or by NaOH treatment to increase the negative charge on the cell surface [58], or by acid to make the actives sites open for adsorption [163], or by Ca^{2+} solution treatment in order to enhance the ion exchange [83]. One of the examples of algal biomass chemically modified used in the biosorption process, is the one obtained after the crosslinking with epichlorohydrin and oxidizing by potassium permanganate. In this approach, *Laminaria japonica* has undergone a chemical modification by crosslinking treatment (Fig. 8.3), and before processing to this step, the biomass selected for lead sorption uptake experiments was first: dried in an oven at 40 °C until constant weight, ground and then sieved into a fraction 0.30–0.4 mm. 10 g of the prepared biomass was made in contact with dimethyl sulphoxide

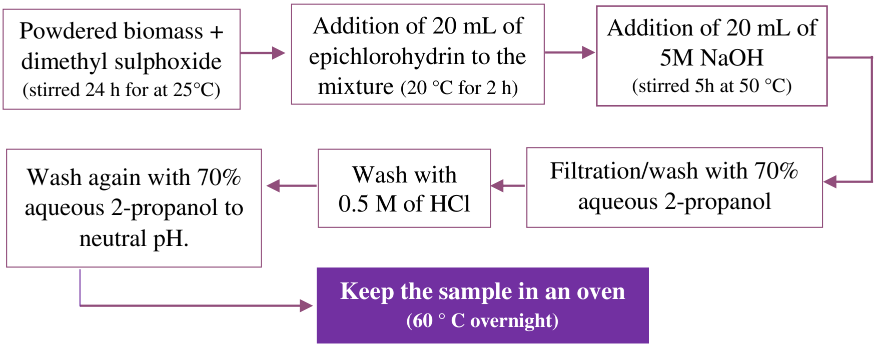


Fig. 8.3 Crosslinking with epichlorydrin of *L. japonica* biomass

(DMSO) to expose the hidden metal-binding groups before crosslinking. Then, the diluted 2-propanol was added to remove DMSO and epichlorohydrin excess [98].

Macroalgae can be crosslinked using other reagents as well. Crosslinking of the raw brown alga *Ascophyllum nodosum* with bis(etheny1) sulfone reagent proved to increase the sorption capacity of the biosorbent material due to the sulfone group's incorporation. In addition, this treatment has been shown to improve algae's physical properties, such as strength, hardness, and swelling characteristics without adversely affecting the sorption [64].

Deniz and Karabulut [34] used various macroalgae, *Polysiphonia sp* (red algae), *Cystoseira sp* (brown algae), and *Chaetomorpha sp*, *Ulva sp* (green algae) and *Cystoseira sp* (brown algae) to prepare a unique adsorbent, the biomass after having undergone a preparation step (washing, drying, sieving), it was treated with a NaOH solution before testing its behavior regarding the elimination of zinc. The adsorbent prepared from various types of macroalgae was judged to have a great potential for the uptake of zinc ions from aqueous solution. The maximum adsorption capacity of zinc was found to be 115.198 mg/g and obtained under some optimal physicochemical parameters (Table 8.5).

Among the interest of researchers is to compare the biosorption behavior of macroalgae and understand the main causes behind their differences in regard to the elimination of heavy metal ions. In this approach, Hamdy [60] used three brown macroalgae *Turbinaria decurrens*, *Cystoseira trinode,* and *Sargassum asperifolium*, and one red alga *Laurencia obtusa* to test their adsorption ability towards Cr^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Cd^{2+}. The prepared algal samples were then treated with chloridric acid until evolution of CO_2 to remove calcium carbonates present in the algal cell matrix before being used in the adsorption study. Compared with the good adsorption capacities of the algae tested without HCl treatment for the elimination of different metal ions, the treated algae showed a low capacity, especially for Cr^{3+} adsorption with *Laurencia obtusa*, where there was practically no adsorption and that was explained to the loss of $CaCo_3$ and the pH of the solution.

8.5 Maximum adsorption capacities (mg/g) for the biosorption of metal ions on macroalgae

Macroalga	Biosorbent	Ion	pH	T (°C)	q $_{max}$ (mg/g)	References
Callithamnion corymbosum sp	Raw alga	Cu(II)	4.4	25	47.6	Lucaci et al. [97]
	Iron nanoparticles /Alginate	Cu(II)			52.6	
	Waste alga	Cu(II)			83.3	
	Alginate	Cu(II)			166	
Undaria pinnatifida	Alga physically modified	Cu(II)	4.5–5.5	20	126	Cho et al. [29]
		Cu(II)			14	
Cystfoseira barbata	Raw alga	Cu(II)	–	25	279	Trica et al. [154]
	Raw alga	Pb(II)			69.3	
	Alginate	Cu(II)			454	
	Alginate	Pb(II)			107	
Hydroclathrus clathratus	Waste	Cd(II)	6.2	25	96.5	Soliman et al. [144]
		Cu(II)			43.4	
Jania rubens	Raw alga	Co(II)	5	25	32.6	Ibrahim [68]
		Pb(II)			30.6	
		Cr(III)			28.5	
		Cd(II)			30.5	
Pterocladia capillacea	Raw alga	Co(II)	–	–	52.6	Ibrahim [68]
		Pb(II)			34.1	
Corallina mediterranea	Raw alga	Co(II)	–	–	76.2	Ibrahim [68]
		Pb(II)			70.3	
		Cr(III)			64.3	
		Cd(II)			64.1	
Galaxaura oblongata	Raw alga	Co(II)	–	–	74.2	Ibrahim [68]
		Pb(II)			105	
		Cr(III)			88.6	
		Cd(II)			85.5	
Schizomeris leibleinii	Raw alga	Cu(II)	6	25	55	Tavana et al. [150]
Undaria pinnatifida	Alga chemically modified	Pb(II)	5.5	25	980	Kim et al. [79]
Syzygium cumini L	Raw alga	Zn(II)	6	-	35.8	King et al. [80]
Ulva fasciata sp	Raw alga	Zn(II)	30	5	13.5	Kumar et al. [86]

(b) Physical Modifications

Chemical modification is not the only option to improve the properties of biosorbents, physical modification has also been used to some extent. One of the main examples of this type of modification is physical activation. This treatment is based on the elimination of a large amount of internal carbon mass, which is a necessary step to obtain a well-developed carbon structure. While, in chemical activation, all the chemicals employed are dehydrating agents that affect pyrolytic decomposition and prevent tar formation, thus, enhancing the yield of carbon [13]. The production of an activated carbon by the physical activation includes a high temperature around 1100–1250 K, this processing can be carried out on the basis of steam, carbon dioxide, and air, or a combination of these [131]. The physical activation takes place in two main steps: the first is a pyrolysis step of the carbon product with a temperature ranges from 300 ˚C to 500 ˚C. At this first stage, the resulting char has a porosity not well developed. The second step is to attack the char with steam or carbon dioxide with a temperature of 900 ˚C–1000 ˚C. This step allows the porosity to develop completely [6]. This kind of modification has been the subject of some published studies and this is perhaps due to its remarkable influence on the adsorption capacity of bioadsorbents prepared from macroalgae and other biomasses regarding inorganic and even organic pollutants [13, 29, 65, 78].

Cho et al. [29] evaluated the adsorption characteristics of charcoal derived from the brown macroalga *Undaria pinnatifida* in the removal of copper from aqueous solution. The charcoal was physically and chemically modified to compare the effect of the chosen modification method on the capacity of the prepared biosorbent to remove copper ions. This study demonstrated the effectiveness of using the physical activated char prepared from seaweeds (Fig. 8.4) in the adsorption of Cu^{2+}, which is higher even than that activated as a result of the chemical process (activation by KOH). The physically activated char showed a great adsorption capacity toward Cu^{2+}. As well as, the authors have explained the low adsorption capacity of char prepared through the chemical activation by the low amount of exchangeable cations, and this was due to the use of an alkaline solution, which decreased the adsorption capacity. The activation by KOH contributes to the removal of the exchangeable alkali or alkali earth metals. The authors noted that the ion exchange might be the main mechanism

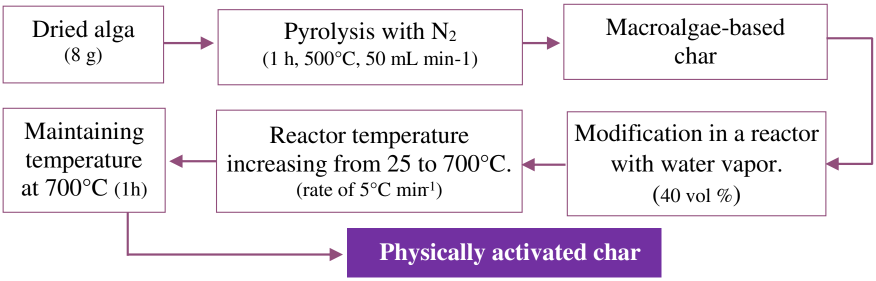


Fig. 8.4 Physical activation of char is derived from *U. pinnatifida* biomass

involved in the removal of copper ions. Also, it was suggested that the heavy metal ion removal procedure using biochar takes place in two steps, the first being the adsorption that takes place in the porous structure of this biosorbent. While, in the second step the ion exchange occurs [142].

6.2.3 Macroalgae Biopolymers

Agar, carrageenan, and alginates are seaweeds hydrocolloids and the most recognized constituents of the algae cell wall. The term "hydrocolloid" refers to any substance allowing the formation of colloidal systems in the form of a gel or sol system of solubilized particles when it is in contact with water [129]. This section focuses mainly on the alginates and carrageenans, which are biopolymers extracted from seaweeds very suitable for the removal of heavy metal pollution. Carrageenans are isolated from the cell wall of red algae, while alginates are obtained from those of brown algae.

(a) Alginic acid and Alginates

Alginic acids are ionic polysaccharides and are abundant in the brown algae cell walls [41]. These polysaccharides belong to a family of copolymers of b-D-mannuronic acid (M) and a-L-guluronic acid (G) [87]. The content of these polysaccharides in the biomass can reach 40% of the dry weight; this strongly depends on two main factors, namely the species and growth conditions.

Alginate is a salt of alginic acid that refers to the common name given to the family of linear polysaccharides containing 1,4-linked b-d-mannuronic (M) and a-l- guluronic (G) [32, 82]. Apart from seaweeds, some microorganisms are able to produce alginates as well, such as *Azotobacter vinelandii* and some strains of *Pseudomonas* [57]. The extracts of brown seaweeds containing alginates were not sold as thinking and gelling agents until 1930s [82]. The total world production of this polymer was estimated to be around 30 000 million/year [57]. The difference between alginic acid and alginate can be observed in their chemical structures (Fig. 8.5).

The functional groups that are most abundant in brown algae are carboxylic groups present in alginate polysaccharides, they are responsible for the ion exchange capacity and that of adsorption [136]. These hydrocolloids that are currently used in various domains, have a high degree of physicochemical heterogeneity, which affects their quality and determines their possible applicability.

Sodium and calcium alginate are the main known forms of alginic salts extracted from macroalgae, and the difference between these salts depends mainly on the nature of the reagent used during the extraction step. The adapted method to extract sodium alginate by several researchers is that developed by Calumpong et al. [24] with some slight modifications [42, 158]. In accordance with this procedure, 25 g of the dried algae is soaked in 800 mL of 2% (v/v) formaldehyde under steering at room temperature for 1 day to remove phenolic compounds and pigments. Later, the sample is thoroughly rinsed with water, then added to 0.2 M hydrochloric acid

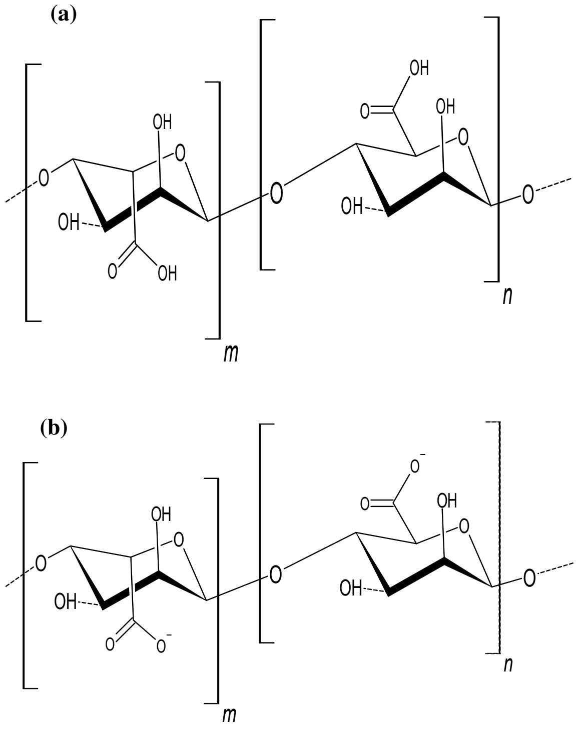


Fig. 8.5 **a** Chemical structure of alginic acid, **b** Chemical structure of sodium alginate

(800 mL) and soaked overnight in HCL. Then, washed with pure water and start the extraction step with the addition of 2% Na_2Co_3 during 3 h at 100 °C. After this time, the mixture is centrifuged (10,000 × g, 30 min) to separate the soluble fraction from the obtained mixture, while the polysaccharides are precipitated by 3 volumes of ethanol 95% (v/3v). Then, the collected sodium alginate is washed twice by 100 mL of acetone, dried at 65 °C, dissolved again in 100 mL of pure water, and before drying the alginate at 65 °C, it was first reprecipitated with ethanol (v/3v). The different steps of sodium alginates extraction are listed in Fig. 1.6.

The difference between the alginates obtained from different sources is in their guluronic (G) and mannuronic (M) residues and the length of each block [88]. These extracts can exist in different forms, which do not have the same properties. Sodium alginate is soluble in water, but calcium alginate can only be soluble if it is dissolved in an alkaline medium because of their physico-chemical and rheological properties. This polymer has a selective affinity toward the cations according to their nature. This affinity depends on some factors including the composition of alginate and electrostatics forces [3]. Physicochemical and rheological properties of the polymer are influenced by the composition in terms of G and M. In addition, the M/G ratio, which ranges between 0.25 and 2.25, allows to appreciate the quality of the alginate. This ratio varies depending on two important factors: the season and the type of the brown alga specie [104]. For instance, the alginate M/G of *Laminaria digitata*,

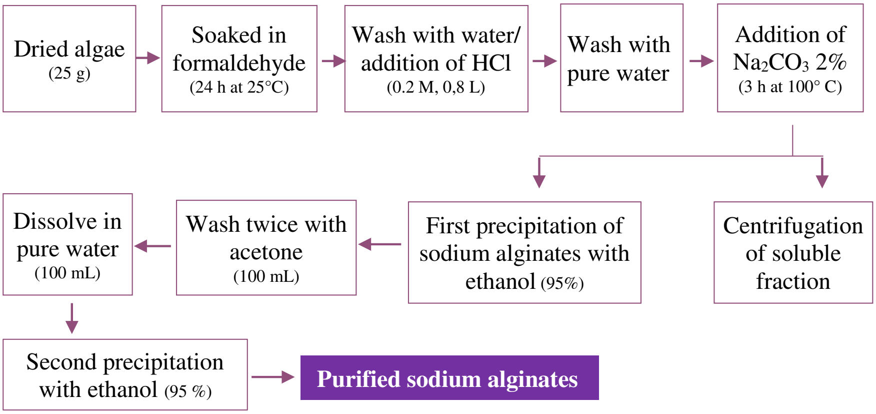


Fig. 8.6 Extraction of sodium alginates from a brown macroalga

Laminaria longicruris, Ascophyllum Nodosum, Macrocystis Pyrifera, Fucus Serratus is 1,44; 2,03; 1,77 1,56; and 1,06, respectively [130]. M/G is calculated using the below equation [55]. Alginates are widely used as additives and ingredients in the food industry [52]. Furthermore, the appreciated extract alginate in food applications is that rich in G acid thanks to its ability to form a gel.

$$\frac{M}{G} = \frac{1 - F_G}{F_G}. \tag{8.3}$$

where M: mannuronic acid, G: guluronic, and F_G represent the mole fraction of G.

After the extraction, the characterization step of the isolated alginate is essential. In sum, the techniques employed for this purpose are: (i) FTIR spectroscopic analysis that is used to show characteristic peaks corresponding to the various groups present in the alginates extracted from seaweeds. It was recommended to quasi-quantitatively determine the M/G value in alginates by measuring the ratio of the absorption band intensities at 808 (M) and 787 cm^{-1} (G) in the infrared spectra [156]. (ii) NMR spectroscopy; this technique of characterization is considered as the most reliable method for the determination of the structure and composition of alginates [20]. The information acquired by this analysis in terms of the uronic acid composition of the alginate allow the calculation of the ratio Mannuronic acid/Guluronic acid (M/G) [55] as well as the distribution of M and G units throughout the polymer chain [146]. (iii) Reological analysis: this technique allows to measure the viscosity of alginate extract using a rheometer with a Peltier temperature control system at 25 °C [40].

Classical methods of alginate extraction seem to present certain disadvantages as they can alter the chemical structure of the biopolymer [164]. Therefore, this situation has pushed some researchers to look for other effective techniques, which do not affect the physicochemical properties, especially if these alginates extracts are made for future pharmaceutical or medical application. Ultrasound-assisted extraction is a process that does not affect the chemical structure of the biopolymer and its molar mass distribution, and it also allows to reduce the extraction time [164].

Apart from its use in the removal of heavy metals, sodium alginate obtained from brown seaweeds exhibits various biological properties, such as antitumour and anti-inflammatory activity [119]. As well, alginate was described as a smart polysaccharide. More information on alginate can be found in a good discussion on the smarter behavior of this polymer and its applications; carried out by Gupta and Raghava [57].

There is a wealth of literature on the use of alginates derived from brown algae to remove heavy metal ions from aqueous solution [32, 38, 97, 118]. The huge exploitation of this algae class may be explained by their performance toward these cations, which is generally better than it is of other seaweeds divisions because of the strong presence of carboxyl groups [136]. It was proved that these linking groups can be increased by an oxidation of marine macroalgae with potassium permanganate. Moreover, this treatment is considered to be one of the main means of increasing the number of carboxylic groups of alginic acids. Consequently, the adsorption behavior of this biomass increases [98]. The evaluation of this behavior in the raw brown alga *Cystoseira barbata* and in its alginate extract regarding the removal of Cd(II) and Pb(II) was the aim of a study conducted by [154]. According to this research, *C. barbata alginate showed* a good performance, and the ratio M/G was found to be 0.64, this normally indicates the dominance of block G over M. Regarding the adsorption capacity, the alginate beads prepared from *C. barbata* showed a maximum adsorption capacity of 454 mg/g for Pb^{2+} and 107 mg/g for Cu^{2+}. These capacities were found to be higher even than those obtained when *C. barbata* was used as adsorbent at its raw form. The obtained adsorption capacities of raw alga toward Cu^{2+} and Pb^{2+} are 279.2 mg/g and 69.3 mg/g, respectively.

Sodium alginates as adsorbents are usually undergoing an essential chemical modification during their preparation, due to the high solubility and weak chemical resistance. This treatment consists of surface grafting and crosslinking [51]. As well as, it was reported that the alginate extracted from *Laminaria digitata* in the form of calcium alginate beads has a high copper and cadmium uptake capacity compared with other bioadsorbents. This is usually due to its high M/G ratio [118]. One of the solutions to overcome the difficulties of adsorbent materials based on sodium alginates, such as their hard structure, limited solubility and high viscosity of their solution, is to compositing them with those with suitable low viscosity and rotation of chains such as poly(vinyl alcohol). Ebrahimi et al. [38] prepared poly(vinyl alcohol) and sodium alginate composite nanofibers (PVA/SA) through the electro spinning method to remove cadmium ions from aqueuse solution. The maximum adsorption capacity related to the use of this adsorbent is 93.163 mg/g, which was obtained with Langmuir model and under optimal experimental conditions.

Brown algae are not the only class from which alginates can be extracted, in 1982, alginates were unexpectedly detected in one of the calcareous red algae species belonging to the *Corallinaceae* family [156]. Therefore, this discovery has encouraged the researchers to focus on the red algae species as a source of extraction of these polysaccharides. In this approach, and for a better valorization of marine resources, a recent study conducted by Lucaci et al. [97] has been carried out on the extraction of alginate from red alga *C. corymbosum sp*, in order to test its potential as biosorbent toward the removal of Cu(II) ions. The maximum adsorption capacity found based on the Langmuir model is 166.66 mg/g reported with the use of *C. corymbosum sp* alginate as adsorbent. Adsorption process of Cu^{2+} was 10 times higher than when using raw algae as the adsorbent. The scanning electron microscope (SEM) characterization of the alginate showed a porous structure and opening shapes. Furthermore, FTIR spectroscopy indicated that the alginate extracted from the raw alga has a large number of functional groups on its surface compared with the all adsorbent materials investigated.

A pre-extraction step has been recommended in order to obtain a high viscosity of alginate, in which the alga is treated with 0.1% formaldehyde overnight and then washed once using hydrochloric acid at pH 4 in a batch system with continuous stirring lasting 15 min [62]. It was found that the alginate presents in algae biomass cannot be all precipitated, but there is a significant amount still after the separation and the precipitation steps due to its high solubility in water [42]. In this context, and in order to not lose soluble alginate, Lucaci et al. [97] proposed the iron nanoparticles functionalized with this polymer as adsorbent to test its behavior with regard to the elimination of copper ions contained in the aqueous solution..

(b) Carageenans

Carrageenans are a group of linear sulfated polysaccharides obtained by extraction from certain species of red algae [155]. Carrageenan is composed of β-1,3 D-galactose and α-1,4 D-(anhydro) galactose and contains about 24% ester sulfate. There are different types of carrageenan, which depends on the number and the position of sulfate group. Carrageenan is divided into variety of types, such as lambda, kappa, iota, theta, and mu carrageenan, and all containing 22–35% of sulfate groups. This classification has been developed on the basis of the solubility of this polymer in potassium chloride [109]. The chemical structure of some of these carrageenans, as well as that of agarose, is shown in Fig. 8.7 [18, 109].

The world production of carrageenan is estimated at 16,500 ton/year, and only commercially available forms are kappa, iota, and lambda carrageenan [130]. Kappa-carrageenan is distinguished from agarose, which is a sulfated polysaccharide of brown algae by the configuration of the a-linked galactose residues and by the presence of one sulfate substituent at C_4 on the b-linked D galactose residues (Fig. 8.7). Related to their rheological properties, agarose gives rigid and turbid gels, while κ- and ι-carrageenans form clear gels [130]. The rigidity of the gels is directly related to the molecular structure and decreases when the sulfate content increases [130]. Carrageenan is widely used as texturing and moisturizing agents in various industries and its use depends mainly on its rheological properties [18, 109].

Carrageenan can be isolated from red algae by the following two main steps; the first is the extraction step using chemicals, such as strong bases KOH and NaOH, the second is alcohol precipitation with ethanol, and then the carrageenan yield is separated from the ethanol–water mixture by a filtration membrane [155]. The precipitation can be also conducted using isopropyl alcohol [130]. Despite the emphasis on the

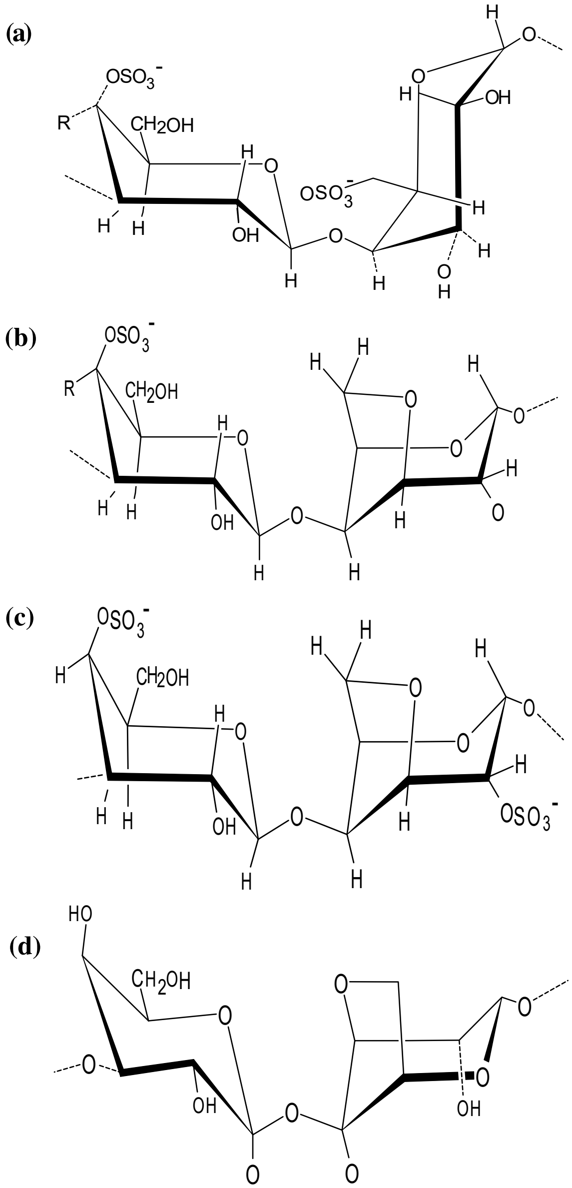


Fig. 8.7 (**a**) Chemical structure of μ-carageenan, (**b**) Chemical structure of k-carrageenan, (**c**) Chemical structure of i-carrageenan, (**d**) Chemical structure of agarose

extraction of carrageenan from algal biomass, its direct use in wastewater treatment whether laden with organic or inorganic pollution, remains poorly documented. Thus, more research is needed on the use of carrageenan prepared from red macroalgae as a natural sorbent. Contrariwise, commercial grade carrageenan is well used as materials to prepare effective adsorbents for organic and inorganic pollutants removal [1, 92, 94, 100, 105]. Biopolymers such as carrageenans have often been considered as adsorbents for removing metals from solution, which is mainly explained by their intrinsic properties in which several functional groups have a significant role [145]. Specifically, hydroxide and sulfate groups have been reported as dominant binding groups in this polymer that are involved in the adsorption process.

6.2.4 Macroalgae Waste

Several studies have focused on the removal of heavy metals using agricultural and industrial wastes, such as coal ash, rice husk, activated carbon [66, 73, 160]. In this regards, algal marine macroalgae as adsorbents have also been widely studied and appreciated. As well as, it was recommended that these biomaterials undergo modifications and be treated with specific chemicals to increase their adsorption capacity and make their surfaces more reactive [136].

The macroalgal waste from alginate extraction is a valuable biomass that can be used as an adsorbent to remove Cu^{2+} from aqueous solution. A recent study conducted by Lucaci et al. [97] proved that waste resulting from the alginate extraction process contained in the marine red alga *C. corymbosum sp* can be successfully used in the removal of these ions with a considerable maximum adsorption capacity of 83.33 mg/g. In fact, this capacity was found to be higher even than it's of the raw alga and the composite material (iron nanoparticles functionalized with alginate). In the same approach, Soliman et al. [144] studied the residue of *Hydroclathrus clathratus* after extracting most of its phytochemicals. The adsorption capacities of the prepared adsorbent from this alga were 96.46 mg/g and 43.4 mg/g for Cd^{2+} and Cu^{2+}, respectively.

7 Concluding Remarks

This chapter has highlighted the possibility of using marine macroalgae as inexpensive bio-adsorbents to reduce and remove heavy metal ions from industrial wastewater, and through our humble analysis of the data reviewed in this topic, the following remarks can be made:

- Seaweeds showed a great capacity to eliminate these inorganic pollutants from water, thus, they can be used as adsorbents.
- Alginate and carrageenan have turned out to be the main polymers responsible for the selectivity of macroalgae for these ions removal, due to their active binding sites, such as carboxylic, sulfonic, and hydroxyl groups.
- Therefore, a particular attention should be paid to the determination of the chemical and structural composition of algae, because it is a crucial step to which any

researcher has to proceed before considering applying these algae in the biosorption process or in any other field, and such information makes it possible to find out which category of algae is more suited to the removal of these ions.

- The great diversity and rich composition of this biomass may lead to the discovery of many new algal bioproducts and processes in the future with potential removal rate of metal ions.
- Also, the use of this resource in the field of biosorption has been seen as a promising solution to the high cost associated with the traditional technologies currently used to treat polluted effluents.
- Even if the number of attempts concerning the removal of these micropollutants by dead marine algae, but still poorly treated their application in the treatment of industrial wastewater.
- Despite the satisfactory results of algal biosorbents in removing heavy metals, there is still a need to develop from this biomass effective and suitable sorbents for the treatment of industrial wastewater containing various types of inorganic impurities.

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