Chapter 16

Metal Removal by Seaweed Biomass

Claudia Ortiz-Calderon, Héctor Cid Silva and
Daniel Barros Vásquez

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/65682

Abstract

Environmental metal pollution is a serious public problem, and it has become an issue leading to research in the effluent remediation area. Techniques involving biosorption processes have been found to be promising due to the low cost of nonliving biomaterials, which have the potential to adsorb metal ions from wastewaters. One of the most promising types of biomasses to be used as biosorbents is the seaweed biomass, particularly from brown algae. The biosorption capability of the seaweed biomass relies on their cell wall chemical composition, mainly composed of alginates and fucoidans, molecules with a high presence of functional groups that interact with metal ions. This book chapter focuses on the use of seaweed biomass for metal biosorption and the chemical basis underlying the process. The current state of the commercial status of biosorption technology based on seaweed biomass is presented. Examples of complementary uses of the algae biomass other than industrial wastewater cleaning processes are presented, and the potential reuse of the biomass after the biosorption focused on biofuel production is discussed.

Keywords: seaweed biomass, metal removal, biosorption, biosorbent, wastewater treatment

1. Introduction

Environmental metal pollution is a serious public problem, and it has become an issue, leading to research in the effluent remediation area. Many techniques have been reported for removing metals from solutions, such as chemical precipitation, adsorption, ion exchange, filtration, chemical oxidation or reduction, electrochemical treatment, membrane processes, and evaporation. It has been found that these methods are limited, because of high operational costs, especially when the initial metal ion concentrations are at the range of 10-100 mg/L [1]. Hence,

INTECH
open science | open minds

techniques involving biosorption processes have been found to be promising, due to the low cost of nonliving biomaterials, which have the potential to adsorb metal ions from wastewater.

The biosorption processes occur when metal ions interact with the functional groups present in biopolymers that are part of the biomass. Chemical groups such as amide, hydroxyl, carboxylate, sulfonate, phosphate, and amino are responsible for the quantitative adsorption of metals [2]. Several interaction mechanisms such as complexation, coordination, chelation, ion adsorption, cation exchange, and microprecipitation have been proposed as the participants in the metal biosorption processes [3].

A wide variety of biomasses has been found to be capable of sequestering metal ions from dilute solutions. An interesting approach is the use of the nonliving forms of the biomaterials because they do not need nutrition for the maintenance and avoid metal toxicity problems [4]. One of the most promising types of biomasses suitable for their use as biosorbents is marine algal biomass (seaweeds), which exhibit a high abundance in the oceans [5].

The biosorption capability of algae biomass is mostly related to their cell wall chemical composition, which exhibits a fiber-like structure and an amorphous embedding matrix of polysaccharides such as alginates and fucoidan [6]. In brown algae, alginates have a high affinity for divalent cations and sulfated polysaccharides give account of the uptake of trivalent cations [7]. The physical and chemical nature of the interaction between the metals and the functional groups present in the biomass has been intensively studied, in order to develop technologies for the sequestration of metals to clean, or to recover, valuable metals from industrial effluents [5, 8, 9].

This book chapter focuses on metal biosorption by seaweed biomass and the chemical interactions between the functional groups of this biomass and the cations. To the end, the potential uses of algae biomass in industrial wastewater cleaning processes and its potential reuse are highlighted.

2. Seaweed biomass

Algae are autotrophic organisms that contain chlorophyll and carry out oxygenic photosynthesis; they are widely distributed and have great diversity. Algae do not represent a formal taxonomic group of organisms, but a highly heterogeneous collection of organisms of different evolutionary lineages and high genetic diversity, which is reflected in the huge diversity that algae in morphological terms, ultrastructure, ecological, biochemical, and physiological [10].

Macroalgae, or seaweed, are a group of fast-growing aquatic organisms including about 9000 species. They are commonly classified into three groups according to the color of the thallus, which correspond to the Chlorophyta (green algae), Rhodophyta (red algae), and Heterokontophyta phylum, class Phaeophyceae (brown algae) [11] (**Figure 1**).

The taxonomic classification of these organisms involves much more than this simple designation and is performed considering a combination of features, including the nature of photosynthetic pigments; polymers present in the cell wall and cellular organization. Today,

Figure 1. Brown algae *Durvillaea antarctica*. Left, a specimen freshly collected from the coastal line. Right, a sample of milled *Durvillaea antarctica* biomass with a size of 500–1000 μm.

thanks to molecular systematics, a good progress has been made in the classification of these organisms, solving the problem of underestimation of diversity when considering only morphological characters [12]. There is great interest in the commercial use of the chemical constituents present in the seaweeds, in the field of energy production, agriculture, food, environmental, and pharmaceutical industry. The global harvest seaweed for food and algal products (e.g., Agar, alginates, and carrageenan) exceeds 3 million tons per year, with a potential harvest estimated at 2.6 million tons for red algae and 16 million tons brown algae [13]. Of particular interest is the use of seaweed dead biomass as biosorbent of heavy metals in solution. Multiple studies have shown a high sorption capacity and selectivity for different metal cations attributed to the polysaccharides present in their cell walls [4, 5, 8, 9, 14–18]. The basic organization of their cell walls comprises a fibril skeleton mainly composed of cellulose, and an amorphous matrix of sulfated galactans constituted by carrageenans and agar in red algae and alginates or alginic acid and fucoidan in brown algae (**Table 1**). Studies to assess

Division	Common name	Pigments	Storage product	Cell wall
Chlorophyta	Green algae	Chlorophyll *a*, *b*; α-, β- and γ-carotenes, and several xanthophylls	Starch (amylose and amylopectin) (oil in some)	Cellulose (β-1,4-glucopyroside), hydroxyproline, glucosides, xylans, and mannans
Phaeophyta	Brown algae	Chlorophyll *a*, *c*; β-carotene and fucoxanthin and several other xanthophylls	Laminaran (β-1,3-lucopyranoside, predominantly); mannitol	Cellulose, alginic, acid, and sulfated, mucopolysaccharides (fucoidan)
Rhodophyta	Red algae	Chlorophyll *a* (*d* in some *Florideophyceae*); R- and C-phycocyanin, allophycocyanin; R- and B-phycoerythrin. α- and β-carotene and several xanthophylls	Floridean starch (amylopectin-like)	Cellulose, xylans, several sulfated polysaccharides (galactans) calcification in some; alginate in *Corallinaceae*

Table 1. Physical and chemical characteristics of three algal divisions. Adapted from [2].

the biosorption (mass of metal adsorbed by mass of biosorbent) of different metals (Pb, Cu, Zn, and Cd) by seaweed biomasses have shown that the higher sorption capacity is exhibited by brown algae [5, 8, 9, 18].

Phaeophyceae is a large and diverse class of species ranging from small filamentous algae to highly complex organisms up to 60 m long. This class presents 2046 species organized into 20 orders [19]. It is believed that *Phaeophyceae* emerged between 150 and 200 million years ago in a secondary endosymbiosis event, in which a red algae was captured by an ancestral protist [12, 20, 21]. Its characteristic color is given by large quantities of fucoxanthin present in their chloroplasts. The most important algae orders from the point of view of the biosorption are Fucales and Laminariales, presenting species with a greater structural complexity. The components in their cell walls and reserve polymers have been reported as the main cause of its great capacity for immobilization of metal cations. The cell wall structure varies according to the species, age of the population, climate, and geographical location. Fibril wall structure, which provides structural support, is composed of cellulose-like plants, although displayed in a lower portion, occupying from 1 to 8% of its dry weight [21]. Two groups of anionic polysaccharides that provide strength and flexibility to the cell wall are alginates (between 10 and 40% dry weight) and fucoidan (between 5 and 20% dry weight). Mannitol and laminarans represent energy backup products. Other components such as proteins and phlorotannins also contribute but in a lesser way to the biosorption, representing about 5% of the biomass dry weight (**Figure 2**).

The three major components of the cell wall extracellular matrix of brown algae, cellulose, alginic acids, and polymers like mannuronic and guluronic acids, are complexed with light

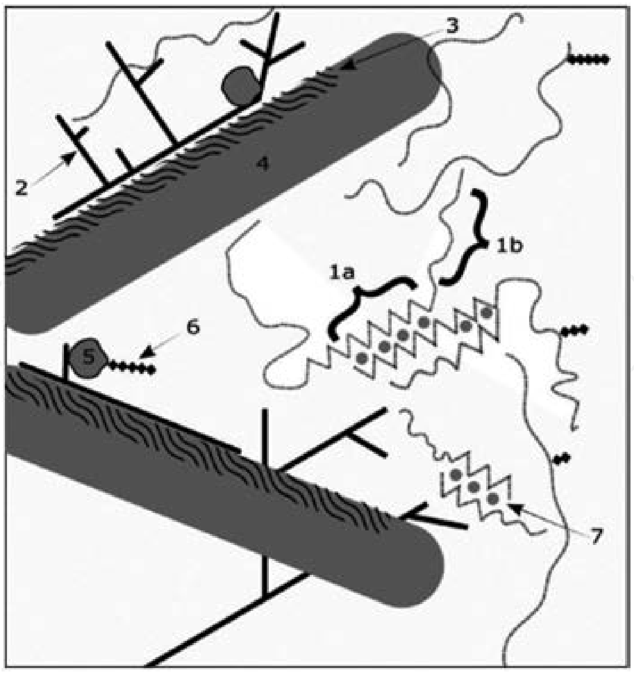

Figure 2. Schematic representation of the main components present in the cell wall of brown algae. Alginates rich in α-1,4-L-guluronate (1a); alginates rich in β-1,4-D-mannuronate (1b); fucoidans (2); hemicellulose (3); cellulose (4); proteins (5); phlorotannins (6); Ca^{2+} (7). Adapted from [2].

metals such as sodium, potassium, magnesium, and calcium, and other polysaccharides [19]. Alginates and sulfated polysaccharides have been reported as the predominant molecular components with reactive groups in brown algae [18]. Biosorption of heavy metals involves several mechanisms that differ qualitatively and quantitatively depending of the chemical species used, the origin of the biomass, and its processing procedure such as reinforcement by crosslinking [20]. Algae biomass possesses several chemical groups that can attract and sequester metals: acetamide, amine, amide, sulfhydryl, sulfate, and carboxyl [2]. This chemical diversity originates a combination of mechanisms for the capture of the metals, including electrostatic attraction, complexation, ion exchange, covalent binding, van der Waals attraction, adsorption, and microprecipitation [3].

Alginates are a family of linear polysaccharides, consisting of two uronic acids units: β-1,4-D-mannuronate (M) and α-1,4-L-guluronate (G). These units are arranged in homopolymer blocks of M, homopolymer blocks of G, and/or heteropolymer blocks of M and G (**Figure 1**). The relative abundance of M and G blocks in the macromolecular structure determines structural properties and affinity of alginates for divalent cations. The affinity of some divalent metal cations varies with M:G ratio [2, 6, 22]. Studies have shown that the affinity of the alginates for cations such as Pb, Cu, Cd, Zn, and Ca increases with a higher content of guluronic acid [23, 24]. The high specificity for divalent cations is explained by the structure of "zigzag" formed by homopolymers of guluronic acid, which stabilizes the Ca^{2+} and other divalent cations easily (**Figure 1**) [2, 22]. Alginates fibers are able to adopt an ordered conformation in solution through dimerization of homopolymeric regions of guluronic acid, in the presence of calcium or other divalent cations, as they are filled with carboxylic groups and other electronegative oxygen atoms. This description is known as the model of "egg box" [25]. The carboxyl groups are the most abundant functional group in brown algae, determined by the percentage of quantifiable sites by titration, reaching about 70%. Furthermore, most of the metal cations of interest show high sequestering at pH near to the dissociation constant (pK_a) of carboxylic acids [2].

Fucoidans are branched sulfated polysaccharides mainly constituted by α-L-fucose, uronic acids, and a small portion of galactose, xylose, arabinose and/or mannose, glucose, and sometimes proteins, presenting an extremely variable molecular weight. They are presented in the form of homopolymers or homofucans called fucans, or heteropolymers called fucoidans. The sulfonate groups in the fucoidans are the second functional group in abundance in brown seaweed, and its role could become prominent, if the binding of the metal occurs at a low pH [2].

Mannitol is a compound derived from monomeric D-mannose present in all brown algae, which can represent up to 30% of the biomass dry weight [2]. The second largest reserve products are laminarans and polysaccharides, which are composed of (1, 3)-β-D-glucans. They consist of residues (1, 3)-β-D-glucopyranose with some 6-O-branches of the main chain. Two types of laminaran chains exist: M, with a mannitol monomer attached to the reducing end, and G, with a glucose monomer attached to the reducing end. All the polysaccharides present hydroxyl groups, but these are less abundant and only are negatively charged at pH above 10, playing a secondary role at low pH [2].

3. Seaweed biomass and metal biosorption

Biosorption of heavy metal ions in wastewater using algae can be ecologically safer, cheap, and efficient. Algae can be used for sorption of toxic and radioactive metal ions [26] and also to recover metal ions like gold and silver [27].

The biosorption of heavy metal ions by seaweed biomass may occur by different mechanisms such as ion exchange, complex formation, and electrostatic interaction [28], being ion exchange the most important [29]. Polysaccharides and proteins present in the algae cell walls provide the metal-binding sites [30]. The sorption capacity of a seaweed cell surface to a specific ion depends on several factors such as the amount of functional groups in the algae matrix, the coordination number of the metal ion to be sorbed, the accessibility of binding groups for metal ions, the complex formation, affinity constants of the metal with the functional group, and the chemical state of these sites [31]. Considering the heterogeneity of the cell wall composition in different seaweed species, the capacity of metal biosorption by the algal strains will vary. For instance, brown algae with alginate in their cell wall composition have a high biosorption affinity for lead ions [5]. Alginate polymers are the primary responsible for heavy metal ions sorption in brown algae, and their capacity to bind the metal directly depends on the number of binding sites on this polymer [32]. In a second place, fucoidans play a key role for heavy metal sequestration.

The functional groups present in the brown and green algae cell wall matrixes, such as carboxyl, hydroxyl, sulfate, phosphate, and amine groups, play a dominant role in the metal binding [30]. The presence of various functional groups and their complexation with heavy metals during biosorption process can be studied by using spectroscopic techniques, such as FT-IR and XPS [33]. The X-ray absorption fine structure spectroscopy and quantum chemistry calculation are also an experimental approach to explain the biosorption mechanisms [34]. An interesting methodology to determine the contribution of different functional groups in the metal adsorption is the derivatization of functional groups, like the pretreatment of the seaweed biomass with methanol in acid media or with propylene oxide, which blocks the action of the carboxyl groups in the biomass [35]. In *Sargassum fluitans*, after 4 h of treatment of the biomass with propylene oxide, about 50% of reduction in the biosorption capacity of Cd and Pb ions was observed [35]. Cid et al. [36] found a 43.3% of decrease in copper biosorption by esterifying biomass of the species *Durvillaea antarctica* using methanol in acid media. The presence of carboxyl, hydroxyl, sulfate, phosphate, and amine functional groups has been found to play a dominant role for the algae-metal interaction by an ion-exchange mechanism that occurs between heavy metals and intrinsic light metals ions such as Ca^{2+} and Mg^{2+}, and Na^{+} and K^{+} [37]. A summary of representative data for efficiency of copper removal for different types of algal biomass is presented (**Table 2**).

Heavy metal ion uptake by algal biomass can be enhanced by physical or chemical treatments that modify the seaweed cell surface structure and provide additional binding sites [32, 41–43]. Physical treatments such as heating/boiling, freezing, crushing, and drying usually lead to an enhanced level of metal ion biosorption. These treatments provide more surface area to increase the biosorption capacity [41] and release cell contents that might bind to

Brown algae specie	pH	q_m (mmol Cu g^{-1} biomass)	References
Ascophyllum nodosum	4.0	0.91	Romera et al. [5]
Durvillaea antarctica	5.0	1.73	Cid et al. [36]
Fucus serratus	5.5	1.60	Ahmady-Asbchin et al. [37]
Fucus spiralis	4.0	1.10	Romera et al. [5]
Fucus vesiculosus	5.0	1.66	Mata et al. [28]
Padina sp.	5.0	1.14	Sheng et al. [18]
Sargassum sp.	5.0	0.99	Sheng et al. [18]
Sargassum sp.	5.5	1.13	Karthikeyan et al. [38]
Sargassum filipendula	4.5	0.89	Davis et al. [39]
Sargassum filipendula	4.5	1.32	Kleinübing et al. [40]
Sargassum fluitans	4.5	0.80	Davis et al. [39]
Sargassum vulgarie	4.5	0.93	Davis et al. [39]

Table 2. Comparison of Cu(II) biosorption maximum capacities of different types of brown algae. Adapted from [36]

metal ions. The most common algal pretreatments are $CaCl_2$, formaldehyde, glutaraldehyde, NaOH, and HCl. Pretreatment with $CaCl_2$ causes calcium binding to alginate that plays an important role in ion exchange [42]. Formaldehyde and glutaraldehyde strengthen the cross-linking between hydroxyl groups and amino groups [43]. NaOH increases the electrostatic interactions of metal ion cations and provides optimum conditions for ion exchange, while HCl replaces light metal ions with a proton and also dissolves polysaccharides of cell wall [32], or denatures proteins, increasing the binding sites for the biosorption process.

4. Industrial uses of seaweed biomass

Over the past four decades, much effort had been devoted to identify readily available non-living seaweed biomass, capable of effectively removing heavy metals, with good hydrodynamic capacities, physicochemical stability, and with the possibility to enhance their capacities to obtain biosorbents. After years of experimentation on hundreds of raw seaweed biomass for biosorption of heavy metals under different conditions, the optimum conditions for the biosorption process at bench scale have been stated for many seaweed biomasses. This research has conducted the efforts to the development of biosorption technologies for industrial applications, considering the volumes and the complex composition of different wastewaters.

One of the most important issues to consider is the biomass organic leaching phenomenon that is produced by the contact of the biomass with the water to be treated, liberating fractions of the biomass, biopolymers, and another chemical compounds. Organic leaching is an important factor to minimize, because it adds organic pollution to the treated water and generates an important biomass loss, resulting in a decrease on the availability of biomass for the next cycle of biosorption [24]. Also, organic leaching provokes hydraulic problems in column systems, because the biomass tends to accumulate at the exit of the packed columns, generating a clot that impairs the normal flow of the treated water passing by the biosorbent bed and generates elevated levels of TDS [44, 45]. The problems of excessive leaching and swelling can be minimized through proper engineering procedures, but the costs and practicability of these procedures are of concern. To control the swelling in seaweed biomass, Chu and Hashim [46] employed polyvinyl alcohol to immobilize biomass of *Sargassum* to construct packed columns. Omar et al. [47] immobilized *Enteromorpha torta* biomass using calcium alginate and solutions of calcium chloride for the biosorption of Cesium-134 on packed column beads. Other authors used calcium or magnesium salts to improve rheological properties of the biomass by the crosslinking generated by calcium ions and the alginate fibers [2], and used this material to make columns beds [48–52]. Other procedures applied to seaweeds biomass to improve the material properties include protonation treatments with different acids: crosslinking with formaldehyde, glutaraldehyde, bis(ethenyl)sulfone, 1-chloro-2,3-epoxypropane and polyethylene imine [14, 53], thermal treatment [54], and chemical modifications of functional groups, among others [55]. It is important to highlight that the costs associated with the raw biomass process and the ultimate disposal of the derived biomass waste should be considered for a viability of installation of the process. One simple way to prevent swelling of seaweeds in packed columns is to mix seaweed biomass with an inert and stable materials such as sand. This will improve the porosity inside the column and thereby enhance the solute flow pattern [56]. The modification of the surfaces of these biosorbents for further removal of other contaminants, for an integral application on wastewater treatment, is rather challenging.

Another important issue to be considered when using biosorbents to treat metal polluted wastewaters is the complexity of the solution, because it can affect the biosorption process by competition for the exchange sites by cationic chemical species other than metals. Vijayaraghavan et al. [57] studied the nickel biosorption capacities on *Sargassum wightii* in aqueous solutions and residual electroplating solutions, finding that the complex nature of electroplating solutions negatively affected the metal biosorption performance, because of the competition with other ions. Patrón-Prado et al. [58] studied the biosorption of cadmium and copper by *Sargassum sinicola* in aqueous solutions and in saline wastewaters, finding that the salinity of the solution caused a reduction in Cd biosorption from 89 to 5.8%. At the same time, the authors found a clear antagonist effect between both metals in solution. The same antagonist effect was reported on other seaweed species [59, 60].

Also, it is well known that most of the seaweed sorbents have poor affinity for anions such as nitrate, sulfate, and phosphate, due to the predominant anionic sites in their surface. These anions are common in effluents and if not removed may lead to eutrophication and other undesirable effects on the environment [61]. Alginates, one of the major constituents of the seaweed biomass, can be chemically modified to remove anionic contaminants from water solutions and can be used to encapsulate materials such as magnetite, leading to the formation of a multifunctional sorbent that has magnetic properties and can remove both cationic heavy metal ions such as copper ions and anionic contaminants, like arsenic [62].

Alginates can be cross-linked by addition of alkaline metals as Ca or Mg [63], resulting in a encapsulation of raw biomass, improving their biosorption capacities, and generating a solid biosorbent with a better hydrodynamic performance. Mata et al. [15] determined the effect of the immobilization of *Fucus vesiculosus* with alginate xerogels in the biosorption of Cd, Cu, and Pb. The immobilization increased the kinetic uptake and intraparticle diffusion rates for the three metals. Song et al. [64] evaluated the recovery of Li, Sr, and La by Ca-alginate beads at different physicochemical conditions, finding the best performance for Sr and La.

The feasibility of the biosorption process to reduce toxic metals presents some limitations, and a fully understanding of the process in the context of a reactor system is necessary. Engineering considerations are crucial when a seaweed-based biosorption system is designed and developed. In general, biosorption systems using dry seaweed biomass correspond to a solid-liquid contact process. This process ideally implies several cycles of biosorption and desorption stages. The effluents to be treated make contact with the biomass in a batch, semi-continuous or continuous flow system. Banks [65] describes different types of reactors with potential use in biosorption system designs: the conventional stirred tank reactors, packed bed reactors, expanded bed reactors, fluidized bed reactors, and airlift reactors, depending on the final result and the type of effluent to be treated.

Despite the considerable progress in the understanding of seaweed biomass interactions with heavy metals made over four decades of continuous research, most seaweed biosorption processes are still at bench scale. Some proposed processes based on biosorption have been patented for commercial applications, some of them at pilot scale and some at commercial scale, mainly represented by units that were constructed in Canada and USA during the 1990s [66]. Thus, only a few industrial processes or products based on biosorption technology have been implemented, especially if we refer only to seaweed applications. A search in WIPO Patentscope (http://patentscope.wipo.int/search/en/search.jsf) only shows 29 patents related to biosorption and heavy metals removal, and only four consider seaweed biomass in the development. Pohl [67] patented a preparation of a biosorbent based on brown algae, consisting in a method to prepare the raw material for biosorption of heavy metals and hydrocarbons to finally obtain a milled dry seaweed biosorbent material. Other inventions include directly applications of seaweed biomass. For example, Volesky and Kuyucak developed a method for the biosorption of gold using seaweed biomass of *Sargassum genus* [68]. In the market, there is a very limited offer on biosorption technologies. Actually, only five products offer a commercial solution to remove pollutants from water. These commercial technologies include AMT-BIOCLAIM™ from Advanced Mineral Technologies, Inc. (AMT), a sorbent obtained from industrial fermentation process by *Bacillus subtilis* [69, 70]. Bio-Recovery System, Inc. (Las Cruces, USA) developed a microalgae biosorbent named as AlgaSORB™, which consists of *Chlorella vulgaris* biomass immobilized on silica gel polymer matrix, to treat heavy metal ions from diluted solutions (1–100 mg g^{-1}). Metagener and RAHCO Bio-Beads have developed two commercial biosorbents, which could be used as effective materials for removal of heavy metal ions from wastewaters (mainly electroplating and mining industry) [1, 71]. Particularly interesting is the invention BV-SORBEX™, by B.V. SORBEX, Inc. (Montreal, Canada), that offers a family of commercial sorbents based on metal-binding biomass, including different-sized powders and granules made of different types of biomass, including seaweeds [72]. These biosorbents remove a wide range of metal ions from diluted or concentrated solutions with high efficiency (over 99%) in a wide range of pH values and aqueous system conditions [73]. However, these products have not been commercially successful [74, 75]. One reason is related to the lack of a full understanding of the mechanisms, kinetics, and thermodynamics of the biosorption process [76]. Another reason is related to the existence of competing technologies based on physical and chemical treatments such as ion exchange, activated carbon, chemical precipitation, oxidation/reduction methods, electrocoagulation, electrodialysis, ultrafiltration, reverse osmosis, and solvent extraction [77]. However, two major arguments that support the biosorption as a convenient cleanup technology are the low cost of the biosorbents and the constant increase in the demands on environmental regulatory standards [61]. Paradoxically, processes to improve the biosorbent performance not only increase the final price of the product but also raise questions about the toxicity and environmental hazards of the final product. All these issues create a need for other commercially attractive applications of biosorption technology. The main suggestion is the use of biosorption for the recovery of precious metals [61, 75]. Future directions may also include a most integrated solution addressed to clean up industrial effluents containing multiple pollutants and the applications of hybrid technologies between traditional and biosorbent technology. Unfortunately, the increasingly published output on the biosorption field do not reflect an improved knowledge of the process, nor aid to commercial exploitation [78]. Biosorptive processes may contribute to primary or secondary biological water treatments including domestic, municipal and industrial wastes, and in some circumstances, solid wastes. Biosorption technology is still on a developing stage, and commercial success will depend on a better understanding of the process, governed by a pragmatic rationale of its commercial development and potential applications.

The final cost of biosorption treatment certainly involves the harvest, transportation, and processing of the biomass, together with the control of optimal conditions of the process, the regeneration of the biosorbent, and the final disposing of the biomass. Other costs usually not discussed are the capital expenses and plant operation costs, because they depend on the design of the treatment plant and the nature of wastewaters to be treated. Because many species of seaweed are valuable for the production of molecules with nutritional value, cosmetic applications among other uses, the use of residual dead biomass is convenient. Preparation of biosorbents is usually a major cost associated with the biosorption process, and biomass preprocessing is necessary to guarantee a good performance of the biosorbent. Thus, much attention should be taken with the estimation of costs, including the final disposal of the residues. Once a biosorbent life cycle ends, the ultimate disposal should be addressed. Landfilling the biomass, chemical or thermal destruction techniques seems an easy way to manage waste biosorbents, procedures that are not cheap or environmentally friendly. Used biosorbents can also be reused for other applications. Therefore, once heavy metal ions are completely removed from the used seaweeds by a demineralization process, they can be used for other applications.

Because the sorption technology based on biomasses has not been fully developed at industrial level, there are scarce data about the technical-economical evaluation of industrial biosorption applications. Some calculations predict that the prices of a biosorbent system represent about a tenth of the price of resins [79]. A comparison between classic methods for metal sorption and biosorption techniques can be summarized considering advantages and disadvantages of different technological approaches (**Table 3**). From the analysis, it can be concluded that biosorption is a clean technology, reducing the amount of solid wastes generated, gives the possibility to recover various metals, and has low operational cost in terms of energy consumption.

Metal adsorption technology	Advantages	Disadvantages	References
Adsorption	High spectrum of pollutants High capacity and fast kinetics Potentially selective	Performance depends on the type of adsorbent Needs chemical or thermal treatment for better performance	Aderhold et al. [80]
Biosorption	High spectrum of pollutants High capacity and fast kinetics Obtained directly from the nature or from industrial waste (low cost)	Poorly selective without chemical modifications	Davis et al. [2]
Chemical precipitation	High spectrum of metals Low cost of implementation Easy operation	High sludge formation implies cost on maintenance and sludge disposal	Rubio et al. [81]
Ion exchange	Metal selective High regeneration capacity	High initial capital and maintenance cost Limited pH tolerance	Rubio et al. [81]
Coagulation/ flocculation	Capacity to reduce biological viability. Good dewatering performance	High cost on chemicals High costs on sludge management	Rubio et al. [81]
Electrochemical precipitation	Applicable for the treatment of heavily contaminated wastes Easy to operate.	High initial capital, high operation cost, and maintenance Need of power energy	Qin et al. [82]
Membrane filtration	Low solid waste generation Low chemical consumption Small space requirement Metal selective method	Temperature instability Low stability at low pH High initial capital, high cost on operation, and maintenance Easy fouling generation and flow stacks	Madaeni and Mansourpanah [83]

Table 3. Comparison of conventional technologies and biosorption for the treatment of metal contaminated waters.

The reuse of seaweed biomass after the remediation process to obtain other products with commercial value is an approach to make more attractive the biosorption process. The usability of the seaweed biomass after the biosorption has several productive destinies. Seaweed biomass residues traditionally are burned, disposed in landfills, or confined, but also can be used to obtain a final valuable product. A new niche of application of the passive biosorption process of metals is the enrichment of biomass with microelements to be used as biological feed supplements and/or fertilizers. Dietary supplements obtained by this way have already demonstrated good results on animals [84, 85]. Micronutrients, such as Cu(II), Mn(II), Zn(II), and Co(III), are usually targets for biosorption on wastewater remediation processes, and a biomass that incorporates these elements allows obtaining a microelements enriched biological material. Seaweed biomass is rich in many nutritional elements such as carbohydrates, proteins, microelements, and polyphenols, representing a natural fertilizer, but is not a full complement to the all requirements to amend poor soils. Different seaweed biomasses were experimented for microelemental enrichment via biosorption, obtaining material to be used as feed additives, to supplement livestock diet [86–88]. It was observed that for all the studied seaweed, the smaller the content of the microelement in the natural biomass, the higher the enrichment coefficient of the biomass reached. Certainly, the difficulty to integrate a wastewater bioremediation process to recover metals and the use of the biomass as a fertilizer or as a feed supplement is that the microelements present in the wastewater are at minimal quantities. Also, the possibility of contamination of the biomass with undesirable elements has to be avoided. Another interestingly approach is the potential use of biomass for biogas production. Seaweed biomass can be anaerobically digested for the production of methane. Nkemka and Murto [89] experimented with the demineralization of seaweed biomass prior fermentative processes, obtaining an efficient production of biogas and at the same time, a residue to be used as a fertilizer. A good demineralization process can produce a useful biomass for composting soils [90]. The same concept would be applied to obtain bio-oils from residual biomass. Diaz-Vazquez et al. [91] evaluated the demineralization of *Sargassum sp*. biomass by several methods before a hydrothermal liquefaction process (HTL) of the biomass to increase the yield of bio-oil production. Algae biomass has a higher energy content than most of the lignocellulosic biomass used for biofuel production [92]. In contrast to the high lignocellulosic contents of terrestrial plants, seaweeds are primarily composed of elastic polysaccharides such as alginic acid, laminarin, carrageenan, and agarose that make them a more suitable feedstock for thermochemical conversion processes. The HTL process converts complex polymers present in the biomass into simpler molecules that can be converted to bio-oils. One major limitation on the HTL process is the high ash content present on seaweed biomass, which reduces the yields an quality of the generated bio-oils, restricting their use in direct combustion or gasification processes [93, 94], so the biomass has to be pretreated to reduce the ash content. Usually, the pretreatment process is carried out with mineral acids like sulfuric acid, nitric acid, or organic acids as acetic acid and citric acid usually in a rate of 10% (w/w) between biomass and acid [56]. The selection of a specific acid for demineralization relies on the mechanisms of removal, the mechanical stability of the biomass, and the final use of the recycled biomass [56]. A proper demineralization process allows the incorporation of seaweed biomass previously used in biosorption processes into a new productive cycle (**Figure 3**). Once the seaweed biomass has been used for the treatment of metal polluted effluents, the treated effluent is recovered, and the seaweed biomass loaded with the metal can be demineralized in situ. By this procedure, a metal-enriched solution can be recovered, and the biomass can be harvested from the container and be submitted to a secondary treatment for further productive processes (**Figure 3**).

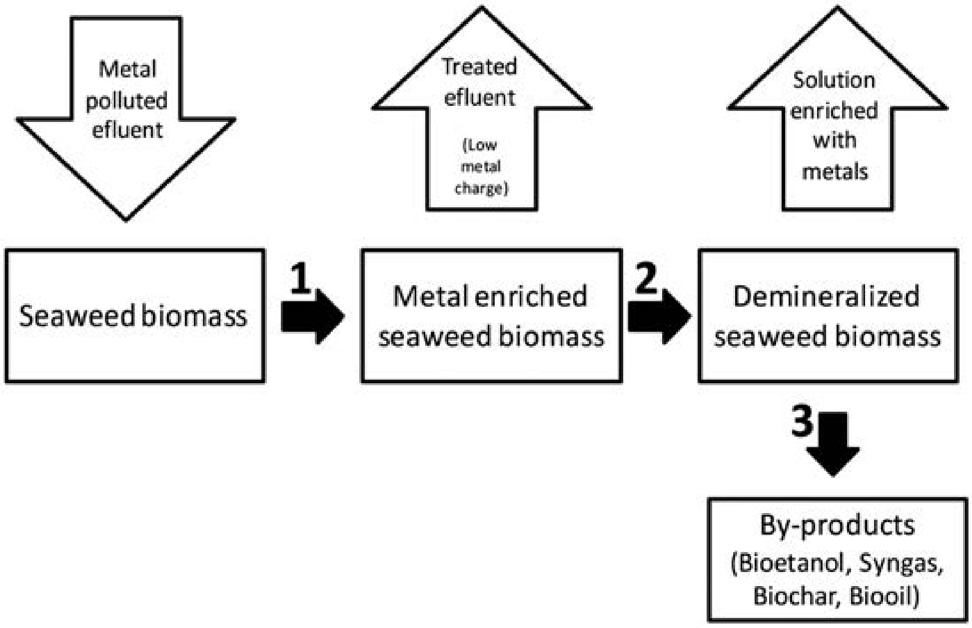

Figure 3. Simplified scheme for industrial use of seaweed biomass. (1) Biosorption process; (2) demineralization process; (3) secondary treatment such as pyrolysis, fermentation, HTL, gasification, among others.

5. Conclusions

A wide variety of biomasses has been evaluated for the sequestration of metal ions from solutions. An interesting approach is the use of the nonliving forms of the biomasses because they do not need nutrition for the maintenance and do not present the problem generated with the toxicity of the metals on living organisms. The biosorption capability of algae biomass is mostly related to the cell wall chemical composition, that is, a fiber-like structure, and an amorphous matrix embedding with polysaccharides such as alginates and fucoidans. In brown algae, alginates have a high affinity for divalent cations and sulfated polysaccharides give account of the capture of trivalent cations. Besides, the reuse of seaweed biomass after the remediation process in order to obtain products with commercial value is an approach that makes attractive the biosorption process at an industrial scale. The chemical composition of brown algae biomass makes it suitable for the production of different by-products such as biofuels, after the biomass has been demineralized. Nevertheless, much more efforts must be done in order to generate quantitative data regarding the performance and the operational costs for biosorption processes using dead seaweed biomass at an industrial level.

Author details

Claudia Ortiz-Calderon*, Héctor Cid Silva and Daniel Barros Vásquez

*Address all correspondence to: claudia.ortiz@usach.cl

Faculty of Chemistry and Biology, Department of Biology, University of Santiago of Chile, Santiago, Chile

References

[1] Atkinson BW, Bux F, Kasan HC. Considerations for application of biosorption technology to remediate metal-contaminated industrial effluents. Water SA. 1998;24(2):129–135.

[2] Davis TA, Volesky B, Mucci A. A review of the biochemistry of heavy metal biosorption by brown algae. Water Res. 2003;37(18):4311–4330.

[3] Raize O, Argaman Y, Yannai S. Mechanisms of biosorption of different heavy metals by brown marine macroalgae. Biotechnol Bioeng. 2004;87(4):451–458.

[4] Jalali R, Ghafourian H, Asef Y, Davarpanah SJ, Sepehr S. Removal and recovery of lead using nonliving biomass of marine algae. J Hazard Mater. 2002;92(3):253–262.

[5] Romera E, González F, Ballester A, Blázquez ML, Muñoz JA. Comparative study of biosorption of heavy metals using different types of algae. Bioresour Technol. 2007;98(17):3344–3353.

[6] Deniaud-Bouët E, Kervarec N, Michel G, Tonon T, Kloareg B, Hervé C. Chemical and enzymatic fractionation of cell walls from Fucales: insights into the structure of the extracellular matrix of brown algae. Ann Bot. 2014;114(6):1203–1216.

[7] Vieira RHSF, Volesky B. Biosorption: a solution to pollution? Int Microbiol. 2000;3(1):17–24.

[8] Murphy V, Hughes H, McLoughlin P. Cu(II) binding by dried biomass of red, green and brown macroalgae. Water Res. 2007;41(4):731–740.

[9] Murphy V, Hughes H, McLoughlin P. Comparative study of chromium biosorption by red, green and brown seaweed biomass. Chemosphere. 2008;70(6):1128–1134.

[10] Rindi F, Soler-Vila A, Guiry MD. Taxonomy of marine macroalgae used as sources of bioactive compounds. In: Hayes M, editor. Marine bioactive compounds: sources, characterization and applications [Internet]. Boston, MA: Springer US; 2012. p. 1–53. doi:10.1007/978-1-4614-1247-2_1

[11] Balboa EM, Conde E, Moure A, Falqué E, Domínguez H. *In vitro* antioxidant properties of crude extracts and compounds from brown algae. Food Chem [Internet]. 2013;138(2–3):1764–1785. doi:10.1016/j.foodchem.2012.11.026

[12] Cock JM, Sterck L, Rouzé P, Scornet D, Allen AE, Amoutzias G, et al. The Ectocarpus genome and the independent evolution of multicellularity in brown algae. Nature. 2010;465(7298):617–621.

[13] Chen JP. Decontamination of heavy metals: processes, mechanisms, and applications. Vol. 97, CRC Press/Taylor and Francis Group; 2012. III–IV.

[14] Holan ZR, Volesky B. Biosorption of lead and nickel by biomass of marine algae. Biotechnol Bioeng. 1994;43(11):1001–1009.

[15] Mata YN, Blázquez ML, Ballester A, González F, Muñoz JA. Biosorption of cadmium, lead and copper with calcium alginate xerogels and immobilized *Fucus vesiculosus*. J Hazard Mater. 2009;163(2–3):555–562.

[16] Rahman MS, Sathasivam KV. Heavy metal adsorption onto *kappaphycus* sp. from aqueous solutions: the use of error functions for validation of isotherm and kinetics models. Biomed Res Int [Internet]. 2015;2015:1–13. Available from: http://www.hindawi.com/journals/bmri/2015/126298/.

[17] Pavasant P, Apiratikul R, Sungkhum V. Biosorption of Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} using dried marine green macroalga *Caulerpa lentillifera*. Bioresour Technol. 2006;97:2321–2329.

[18] Sheng PX, Ting YP, Chen JP, Hong L. Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms. J Colloid Interface Sci. 2004;275(1):131–141.

[19] Guiry MD, Guiry G. AlgaeBase. World-wide electronic publication, National University of Ireland, Galway. [Internet]. 2016 [cited 2016 Jul 8]. Available from: http://www.algaebase.org.

[20] Hamdaoui O, Naffrechoux E. Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon. Part I. Two-parameter models and equations allowing determination of thermodynamic parameters. J Hazard Mater. 2007;147(1–2):381–394.

[21] Michel G, Tonon T, Scornet D, Cock JM, Kloareg B. The cell wall polysaccharide metabolism of the brown alga *Ectocarpus siliculosus*. Insights into the evolution of extracellular matrix polysaccharides in Eukaryotes. New Phytol. 2010;188(1):82–97.

[22] Holan ZR, Volesky B. Biosorption of heavy metals: review. Biotechnol Prog. 1995;11:235–250.

[23] Vierira R, Volesky B. Biosorption: a solution to pollution? Int Microbiol. 2000;3:17–24.

[24] Figueira MM, Volesky B, Ciminelli VST, Roddick FA. Biosorption of metals in brown seaweed biomass. Water Res. 2000;34(1):196–204.

[25] Rowbotham JS, Dyer PW, Greenwell HC, Selby D, Theodorou MK. Copper(II)-mediated thermolysis of alginates: a model kinetic study on the influence of metal ions in the thermochemical processing of macroalgae. Interface Focus. 2013;3:1–16.

[26] Pohl P, Schimmack W. Adsorption of radionuclides (134Cs, 85Sr, 226Ra, 241Am) by extracted biomasses of cyanobacteria (*Nostoc carneum*, *N. insulare*, *Oscillatoria geminata* and *Spirulina laxis-sima*) and Phaeophyceae (*Laminaria digitata* and *L. japonica*; waste products from alginat. J Appl Phycol. 2006;18(2):135–143.

[27] Mata YN, Torres E, Blázquez ML, Ballester A, González F, Muñoz JA. Gold(III) biosorption and bioreduction with the brown alga *Fucus vesiculosus*. J Hazard Mater. 2009;166(2–3):612–618.

[28] Mata YN, Blázquez ML, Ballester A, González F, Muñoz JA. Characterization of the biosorption of cadmium, lead and copper with the brown alga *Fucus vesiculosus*. J Hazard Mater. 2008;158(2–3):316–323.

[29] Michalak I, Chojnacka K. Interactions of metal cations with anionic groups on the cell wall of the macroalga *Vaucheria* sp. Eng Life Sci. 2010;10(3):209–217.

[30] Gupta VK, Rastogi A. Biosorption of lead from aqueous solutions by green algae *Spirogyra* species: kinetics and equilibrium studies. J Hazard Mater. 2008;152(1):407–414.

[31] Mehta SK, Gaur JP. Use of algae for removing heavy metal ions from wastewater: progress and prospects. Crit Rev Biotechnol. 2005;25(3):113–152.

[32] Romera E, González F, Ballester A, Blázquez ML, Muñoz JA. Biosorption with algae: a statistical review. Crit Rev Biotechnol. 2006;26(4):223–235.

[33] Yang F, Liu H, Qu J, Paul Chen J. Preparation and characterization of chitosan encapsulated *Sargassum* sp. biosorbent for nickel ions sorption. Bioresour Technol [Internet]. 2011;102(3):2821–2828. doi: 10.1016/j.biortech.2010.10.038

[34] Zheng Y-M, Liu T, Jiang J, Yang L, Fan Y, Wee ATS, et al. Characterization of hexavalent chromium interaction with Sargassum by X-ray absorption fine structure spectroscopy, X-ray photoelectron spectroscopy, and quantum chemistry calculation. J Colloid Interface Sci [Internet]. 2011;356(2):741–748. doi:10.1016/j.jcis.2010.12.070

[35] Fourest E, Volesky B. Contribution of sulfonate groups and alginate to heavy metal biosorption by the dry biomass of *Sargassum fluitans*. Environ Sci Technol. 1996;30(1):277–282.

[36] Cid H, Ortiz C, Pizarro J, Barros D, Castillo X, Giraldo L, et al. Characterization of copper (II) biosorption by brown algae *Durvillaea antarctica* dead biomass. Adsorption. 2015;21(8):645–658.

[37] Ahmady-Asbchin S, Andrès Y, Gérente C, Cloirec PL. Biosorption of Cu(II) from aqueous solution by *Fucus serratus*: surface characterization and sorption mechanisms. Bioresour Technol. 2008;99(14):6150–6155.

[38] Karthikeyan S, Balasubramanian R, Iyer CSP. Evaluation of the marine algae *Ulva fasciata* and *Sargassum* sp. for the biosorption of Cu(II) from aqueous solutions. Bioresour Technol. 2007;98(2):452–455.

[39] Davis TA, Volesky B, Vieira RHSF. Sargassum seaweed as biosorbent for heavy metals. Water Res. 2000;34(17):4270–7278.

[40] Kleinübing SJ, da Silva EA, da Silva MGC, Guibal E. Equilibrium of Cu(II) and Ni(II) biosorption by marine alga *Sargassum filipendula* in a dynamic system: competitiveness and selectivity. Bioresour Technol. 2011;102(7):4610–4617.

[41] López Errasquín E, Vázquez C. Tolerance and uptake of heavy metals by Trichoderma atroviride isolated from sludge. Chemosphere. 2003;50(1):137–143.

[42] Bishnoi NR, Kumar R, Kumar S, Rani S. Biosorption of Cr(III) from aqueous solution using algal biomass Spirogyra spp. J Hazard Mater. 2007;145(1–2):142–147.

[43] Ebrahimi B, Shojaosadati SA, Ranaie SO, Mousavi SM. Optimization and evaluation of acetylcholine esterase immobilization on ceramic packing using response surface methodology. Process Biochem. 2010;45(1):81–87.

[44] Fosso-Kankeu E, Mulaba-Bafubiandi AF. Review of challenges in the escalation of metal-biosorbing processes for wastewater treatment: applied and commercialized technologies. Afr J Biotechnol. 2014;13(17):1756–1771.

[45] Schiewer S, Volesky B. Ionic strength and electrostatic effects in biosorption of protons. Environ Sci Technol. 1997;31(7):1863–1871.

[46] Chu KH, Hashim MA. Copper biosorption on immobilized seaweed biomass: column breakthrough characteristics. J Environ Sci. 2007;19(8):928–932.

[47] Omar HA, Abdel-Razek AS, Sayed MS. Biosorption of Cesium-134 from aqueous solutions using immobilized marine algae: equilibrium and kinetics. Nat Sci. 2010;8(11):140–147.

[48] Holan ZR, Volesky B, Prasetyo I. Biosorption of cadmium by biomass of marine algae. Biotechnol Bioeng. 1993;41(8):819–825.

[49] Aravindhan R, Madhan B, Rao JR, Nair BU. Recovery and reuse of chromium from tannery wastewaters using *Turbinaria ornata* seaweed. J Chem Technol Biotechnol. 2004;79(11):1251–1258.

[50] Cossich ES, Da Silva EA, Tavares CRG, Filho LC, Ravagnani TMK. Biosorption of chromium(III) by biomass of seaweed *Sargassum* sp. in a fixed-bed column. Adsorption. 2004;10(2):129–138.

[51] Borba CE, Guirardello R, Silva EA, Veit MT, Tavares CRG. Removal of nickel(II) ions from aqueous solution by biosorption in a fixed bed column: experimental and theoretical breakthrough curves. Biochem Eng J. 2006;30(2):184–191.

[52] Tsui MTK, Cheung KC, Tam NFY, Wong MH. A comparative study on metal sorption by brown seaweed. Chemosphere. 2006;65(1):51–57.

[53] Leusch A, Holan ZR, Volesky B. Biosorption of heavy metals (Cd, Cu, Ni, Pb, Zn) by chemically-reinforced biomass of marine algae. J Chem Technol Biotechnol. 1995;62:279–288.

[54] Park D, Yun Y-S, Young Cho H, Park JM. Chromium biosorption by thermally treated biomass of the brown seaweed, *Ecklonia* sp. Ind Eng Chem Res. 2004;43(26):8226–8232.

[55] Park D, Yun YS, Jong MP. Studies on hexavalent chromium biosorption by chemically-treated biomass of *Ecklonia* sp. Chemosphere. 2005;60(10):1356–1364.

[56] Vijayaraghavan K, Balasubramanian R. Is biosorption suitable for decontamination of metal-bearing wastewaters? A critical review on the state-of-the-art of biosorption processes and future directions. J Environ Manage. 2015;160:283–296.

[57] Vijayaraghavan K, Palanivelu K, Velan M. Treatment of nickel containing electroplating effluents with *Sargassum wightii* biomass. Process Biochem. 2006;41(4):853–859.

[58] Patrón-Prado M, Acosta-Vargas B, Serviere-Zaragoza E, Méndez-Rodríguez LC. Copper and cadmium biosorption by dried seaweed *Sargassum sinicola* in saline wastewater. Water Air Soil Pollut. 2010;210(1–4):197–202.

[59] Zhou JL, Huang PL, Lin RG. Sorption and desorption of Cu and Cd by macroalgae and microalgae. Environ Pollut. 1998;101(1):67–75.

[60] Sheng PX, Ting YP, Chen JP. Biosorption of heavy metal ions (Pb, Cu, and Cd) from aqueous solutions by the Marine Alga *Sargassum* sp. in single- and multiple-metal systems. Industrial and Engineering Chemistry Research. 2007;46(8):2438–2444.

[61] Volesky B. Biosorption and me. Water Res. 2007;41(18):4017–4029.

[62] Lim SF, Zheng YM, Zou SW, Chen JP. Characterization of copper adsorption onto an alginate encapsulated magnetic sorbent by a combined FT-IR, XPS, and mathematical modeling study. Environ Sci Technol. 2008;42(7):2551–2556.

[63] He J, Chen JP. A comprehensive review on biosorption of heavy metals by algal biomass: materials, performances, chemistry, and modeling simulation tools. Bioresour Technol. 2014;160:67–78.

[64] Song D, Park S, Kang HW, Park S Bin, Han J. Recovery of Lithium (I), Strontium (II), and Lanthanum (III) using Ca-alginate beads. J Chem Eng. 2013;58:2455–2464.

[65] Banks C. Scavenging trace concentrations of metals. In: Wase J, Forster C, editors. Biosorbents for metal ions. London, United Kingdom: Taylor & Francis Ltd; 1997. p. 115–140.

[66] Tsezos M. Biosorption of metals. The experience accumulated and the outlook for technology development. Hydrometallurgy. 2001;59(2–3):241–243.

[67] Pohl P. Method of production of adsorption material. US patent number 5648313. 1997.

[68] Volesky B, Kuyucak N. Biosorbent for gold. US patent number 4769223. 1988.

[69] Brierley JA, Brieley CL, Goyak GM. AMT-BIOCLAIM: A new wastewater treatment and metal recovery technology. In: Lawrence RW, Branion RMR, Ebner HG, editors. Fundamental and applied biohydrometallurgy. Boca Raton: CRC Press; 1986. p. 291–308.

[70] Brielly J. Production and application of a Bacillus-based product for use in metals biosorption. In: Volesky B, editor. Biosorption of heavy metals. Boca Raton: CRC Press; 1990. p. 305–311.

[71] Chojnacka K. Biosorption and bioaccumulation—the prospects for practical applications. Environ Int [Internet]. 2010;36(3):299–307. doi: 10.1016/j.envint.2009.12.001

[72] Volesky B. Biosorption of heavy metals. In: Volesky B, editor. CRC Press; 1990. 3–5 p.

[73] Bv-sorbex. BV Sorbex Technology Description www.bvsorbex.net/sxProcess.pdf (revised on July 2016).

[74] Vijayaraghavan K, Won SW, Mao J, Yun YS. Chemical modification of *Corynebacterium glutamicum* to improve methylene blue biosorption. Chem Eng J. 2008;145(1):1–6.

[75] Park D, Yun Y-S, Park JM. The past, present, and future trends of biosorption. Biotechnol Bioprocess Eng. 2010;15(1):86–102.

[76] BV SORBEX Inc. BV SORBEX Inc. The company. http://www.bvsorbex.net/sx.htm (revised on July 2016).

[77] Fomina M, Gadd GM. Biosorption: Current perspectives on concept, definition and application. Bioresour Technol [Internet]. 2014;160:3–14. doi:10.1016/j.biortech.2013.12.102

[78] Gadd GM. Biosorption: Critical review of scientific rationale, environmental importance and significance for pollution treatment. J Chem Technol Biotechnol. 2009;84(1):13–28.

[79] Volesky B. Detoxification of metal-bearing effluents: biosorption for the next century. Hydrometallurgy. 2001;59(2–3):203–216.

[80] Aderhold D, Williams CJ, Edyvean RGJ. The removal of heavy-metal ions by seaweeds and their derivatives. Bioresour Technol. 1996;58(1):1–6.

[81] Rubio J, Souza ML, Smith RW. Overview of flotation as a wastewater treatment technique. Miner Eng. 2002;15(3):139–155.

[82] Qin JJ, Wai MN, Oo MH, Wong FS. A feasibility study on the treatment and recycling of a wastewater from metal plating. J Memb Sci. 2002;208(1–2):213–221.

[83] Madaeni SS, Mansourpanah Y. COD removal from concentrated wastewater using membranes. Filtr Sep [Internet]. 2003;40(6):40–46.

[84] Michalak I, Chojnacka K, Witek-Krowiak A. State of the art for the biosorption process—a review. Appl Biochem Biotechnol. 2013;170(6):1389–1416.

[85] Saeid A, Chojnacka K, Korczyński M, Korniewicz D, Dobrzański Z. Biomass of Spirulina maxima enriched by biosorption process as a new feed supplement for swine. J Appl Phycol. 2013;25(2):667–675.

[86] Michalak I, Chojnacka K. Edible macroalga Ulva prolifera as microelemental feed supplement for livestock: the fundamental assumptions of the production method. World J Microbiol Biotechnol. 2009;25(6):997–1005.

[87] Michalak I, Chojnacka K. The application of macroalga *Pithophora varia* Wille enriched with microelements by biosorption as biological feed supplement for livestock. J Sci Food Agric. 2008;88(7):1178–1186.

[88] Michalak I, Chojnacka K. The new application of biosorption properties of *Enteromorpha prolifera*. Appl Biochem Biotechnol. 2010;160(5):1540–1556.

[89] Nkemka VN, Murto M. Evaluation of biogas production from seaweed in batch tests and in UASB reactors combined with the removal of heavy metals. J Environ Manage. 2010;91(7):1573–1579.

[90] Eyras MC, Defossé GE, Dellatorre FG. Seaweed compost as an amendment for horticultural soils in patagonia, Argentina. Compost Sci Util. 2008;16(2):119–124.

[91] Diaz-Vazquez LM, Rojas-Perez A, Fuentes-Caraballo M, Robles IV, Jena U, Das KC. Demineralization of *Sargassum* spp. macroalgae biomass: selective hydrothermal liquefaction process for bio-oil production. Front Energy Res. 2015;3(February):1–11.

[92] Ross AB, Jones JM, Kubacki ML, Bridgeman T. Classification of macroalgae as fuel and its thermochemical behaviour. Bioresour Technol. 2008;99(14):6494–6504.

[93] Bach QV, Sillero MV, Tran KQ, Skjermo J. Fast hydrothermal liquefaction of a Norwegian macro-alga: screening tests. Algal Res. 2014;6(PB):271–276.

[94] Neveux N, Yuen AKL, Jazrawi C, Magnusson M, Haynes BS, Masters AF, et al. Biocrude yield and productivity from the hydrothermal liquefaction of marine and freshwater green macroalgae. Bioresour Technol. 2014;155:334–341.