Chapter 4

Bioremediation of Toxic Heavy Metals Using Marine Algae Biomass

Laura Bulgariu and Dumitru Bulgariu

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Abstract Marine algae are generally considered cheap and available materials, which do not compete with agricultural crops for land or water, and are therefore included into category of renewable biological resources. Currently, the marine algae have several industrial uses linked to biofuel production and the extraction of some important active compounds, but these applications are still limited by several technological difficulties. However, the use of marine algae biomass in the biosorption processes for environmental and wastewater remediation has become increasingly important. It is well known that the heavy metal pollution has severe negative consequences for human health and negative impact on the environment. Therefore, the potential use of marine algae to remove the content of toxic heavy metals, mainly from industrial effluents which are the main sources of environmental pollution, through the development of ecological approaches, has gained a worldwide

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L. Bulgariu (✉)
Faculty of Chemical Engineering and Environmental Protection Cristofor Simionescu,
Department of Environmental Engineering and Management,
Technical University Gheorghe Asachi of Iaşi, Iaşi, Romania
e-mail: lbulg@tuiasi.ro

D. Bulgariu
Faculty of Geography and Geology, “Al. I. Cuza” University of Iasi, Iaşi, Romania

Romanian Academy, Filial of Iasi, Collective of Geography, Iaşi, Romania

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interest. In this chapter, the performances of marine algae biomass as biosorbents for the removal of toxic heavy metals from aqueous media are evaluated, and the main possible practical applications are highlighted. The experimental factors that influence the biosorption capacity of marine algae biomass, as initial solution pH, biosorbent dosage, initial heavy metal concentration, contact time and temperature, are discussed in order to highlight the importance of well-defined experimental conditions for the use of these types of biosorbents. The isotherms and kinetics modelling of the biosorption data was also considered, because the calculated parameters can lead to development of the biosorption systems of toxic heavy metals with high bioremediation potential.

Keywords Toxic heavy metals · Marine algae · Biosorption processes · Environment remediation · Wastewater treatment

4.1 Introduction

The rapid development of industrial activities is the main characteristic of the last century, which has led to an increase in the standard of living of people. Unfortunately, with the development of the industrial sector, many environmental issues have arisen. One of the most important environmental issues is the degradation of the ecosystems' quality due to the presence of hazardous and harmful pollutants, such as heavy metals (Gautam et al. 2015; Naushad 2014). Heavy metals that get to contaminate the environment come mainly from the discharge of improperly treated industrial effluents, and for this reason, industrial activities are still considered to be one of the most important sources of environmental pollution with this kind of pollutants (Wu et al. 2015; Zhang et al. 2018). The global statistics reported by UNESCO (UNESCO 2003) have shown that at the level of 2003, the distribution of water use is 8% in domestic use, 22% in industry and 70% in agriculture. Therefore, an important quantity of water is annually used in the performing of industrial activities, but most important is that a big fraction of this water can be discharged into environment as wastewater and can contribute to environmental pollution.

It is well known that due to their industrial importance, various toxic heavy metals (Pb(II), Cd(II), Hg(II), Cr(VI), etc.) are intensively used in numerous industrial processes from mining industry, plating and smelting industry, fertilizers manufacturing, chemical industry, textile industry, pigments and plastics, etc. (Ghasemi et al. 2014; Mendoza et al. 1998; Lyer et al. 2005; Qaiser et al. 2007), and because they can't be destroyed or degraded and have an accumulation tendency in natural water sources (Volesky and Holan 1995; Qaiser et al. 2007), they have been included into categories of priority environment pollutants. Therefore, the presence of heavy metals in natural water over a maximum concentration level (Aklil et al. 2004; Aydin et al. 2008) affects the human health and decreases the quality of other biological systems, and hence the heavy metals content in the discharged industrial wastewater was established by legislation (AL-Othman et al. 2011).

Based on these considerations, removing heavy metal ions from industrial wastewater is still an important issue, both from an environmental and economic point of view. In this way environmental pollution can be prevented, and the reintroduction of heavy metals (recovered from wastewater) into industrial processes ensures the premises of sustainable development (Judd 2016).

Frequently for the removal of toxic heavy metals from industrial effluents are used methods such as chemical precipitation, coagulation/flocculation, membrane filtration, electrochemical techniques, ion exchange, etc. (Abdolali et al. 2016; Syukor et al. 2016). But, most of the time, these methods are not effective for removing low concentrations of heavy metals or are very expensive due to the high operational costs, high consumption of chemical reagents, or high energy requirements, to which it is added the generation of significant amounts of secondary sludge, which should be also properly treated (Satapathy and Natarajan 2006; Wang and Chan 2009).

Unlike these, biosorption is often considered a low-cost method that offers flexibility in design and operation, can be successfully used to remove low and high concentration of various heavy metals from aqueous effluents in different experimental conditions, minimizes the chemical reagent consumption and production of secondary sludge and allows, in most cases, the recovery of retained metal ions (Davis et al. 2003; Zhao et al. 2011). All these advantages have led to the elimination of heavy metal ions from water effluents through biosorption as an economic and ecological way that respects the principles of sustainable development. However, all these advantages largely depend on the type of biomass used as biosorbent in biosorbent processes (Vijayaraghavan and Balasubramanian 2015). This is why finding materials that are available in large quantities, cheap and easy to collect, and requires only a few stages of preparation is still one of the most important aspects in designing an effective biosorption process (Gupta et al. 2015).

Marine algae meet all these conditions and are considered a promising biological resource because they are available in many regions, do not require special growth conditions, making their productivity high, require only a few simple preparation stages and have high efficiency to retain heavy metal ions from the aqueous solution (Davis et al. 2003; Hannachi et al. 2015; Vijayaraghavan and Balasubramanian 2015). In addition, since the heavy metal biosorption involves a metabolism-independent mechanism in which the metal ions from aqueous media are bound to the surface of the cellular walls (Donmez et al. 1999; Malik 2004; Kumar et al. 2007), it is preferred to use non-viable algae as biosorbents, because they are obtained easier and their cost of preparation is lower. Under these conditions, the marine algae biomass behaves like a chemical substrate where the numerous and varied functional groups are uniformly distributed on the biomass surface, and these will represent the binding sites for the heavy metal ions from aqueous solution.

The presence of cell walls surface of various negatively charged functional groups, such as hydroxyl, carboxyl, sulphydryl, sulphate and amino groups (Donmez et al. 1999; Davis et al. 2003), makes that marine algae biomass to have a high ability to uptake toxic metal ions from aqueous media. These functional groups mainly come from the constituents of marine algae (polysaccharides, proteins, lipids), and therefore their ability to remove heavy metals largely depends on their chemical composition and, ultimately, on their type.

In this chapter, the performances of marine algae biomass as biosorbents for the removal of toxic heavy metals from aqueous media are evaluated, and the main possible practical applications are highlighted. In the analysis of biosorption process efficiency, the main experimental parameters which influence the biosorption capacity of marine algae (such as initial solution pH, biosorbent dosage, initial heavy metal concentration, contact time and temperature) are discussed, as well as the isotherms and kinetics modelling of the biosorption data. All these aspects will highlight the potential of marine algae biomass to retain toxic heavy metals from aqueous media through biosorption, with applications in the environmental bioremediation.

4.2 Sources of Toxic Heavy Metals Pollution

Industrial wastewater containing significant concentrations of heavy metals are produced in large quantities from various industrial activities. This is why the discharge of industrial effluents into the environment without proper treatment remains the main source of environmental pollution with toxic heavy metals (Dixit et al. 2015; Gautam et al. 2015). Thus, electroplating, milling, conversion-coating, anodizing-cleaning, etc. generate significant quantities of wastewater containing cadmium, lead, chromium, nickel, zinc, copper, vanadium, platinum, silver and titanium (Barakat 2011). The printed circuit board manufacturing is another source of wastewater which contains significant concentration of tin, lead, copper and nickel. Inorganic paint manufacturing produces wastewater containing chromium and cadmium compounds. Beside these, other common industrial activities such as energy production or intensive livestock production and aquaculture are responsible by the generation of important quantities of wastewater in which the concentration of toxic heavy metals, such as copper, cadmium, chromium nickel lead, zinc, etc., is significant. Table 4.1 summarizes the quantities of toxic heavy metals released in the

Table 4.1 The quantities (tones) of some toxic heavy metals released into environment from different industrial sectors in 2014 (E-PRTR 2016)

Industrial sector	Cd(II)	Cu(II)	Cr total	Ni(II)	Pb(II)	Zn(II)
Mineral industry	3	115	36	18	43	326
Metal processing	2	19	278	96	33	188
Chemical industry	0.5	13	30	20	10	117
Energy	3	35	21	36	9	0.3
Pulp and paper industry	0.9	14	4	7	3	118
Livestock production and aquaculture	–	69	–	–	–	227
Other industrial activities	0.1	2	32	2	0.3	11

Table 4.2 Examples of toxic heavy metals and their consequences on human health

Heavy metal	Human health consequences (Babel and Kurniawan 2003)	Maximum concentration limit, mg/L[a]	
		NTPA 001/2005	NTPA 002/2005
Cadmium	Kidney damage, renal disorder	0.2	0.3
Copper	Liver damage, insomnia, Wilson disease	0.1	0.2
Chromium	Carcinogenic, diarrhea, headaches	1.0	1.5
Nickel	Dermatitis, nausea chronic asthma	0.5	1.0
Lead	Kidney diseases, circulatory and nervous system damage	0.2	0.5
Zinc	Depression, lethargy, neurological signs	0.5	1.0

[a] Maximum concentration limits according with Romanian regulation (NTPA 001/2005; NTPA 002/2005)

environment from different industrial sectors in 2014, according to the data available from the European Pollutant Release and Transfer Register (E-PRTR).

Heavy metals are included in the category of persistent pollutants because they remain in the environment for a long time and due to the accumulation trend and their toxic effect have serious consequences for human health. In Table 4.2 are mentioned some of the most relevant heavy metals with large industrial applications, which have negative consequences on human health.

In addition, in order to minimize exposure of human and environment to heavy metals, wastewater regulations have been established, which limit the concentration of heavy metals that may be present in the discharged industrial effluents. In Romania, the wastewater regulation has two thresholds for heavy metal concentration, one characteristic for the industrial wastewater discharged into sewerage networks (NTPA 002/2005) and other for the industrial wastewater discharged into natural water sources (NTPA 001/2005). The maximum concentration limits of the some toxic heavy metals in wastewater according with the Romanian regulation are also summarized in Table 4.2.

Therefore, in order to prevent environmental pollution and to respect the principles of sustainable development, it is necessary to remove the heavy metals from industrial wastewater, and, if this is done by a method that allows for their recovery, this activity could have also economic benefits. Biosorption has this possibility, and finding a suitable biosorbent (such as marine algae biomass) will allow the design of a suitable industrial wastewater treatment system to remove toxic heavy metals.

4.3 Preparation and Characterization of Marine Algae Biosorbents

Marine algae are widespread in many regions of the world, being found in coastal areas of the seas and oceans. From biological point of view, marine algae are included in the "plants" category and have dimensions that can range from a few

Table 4.3 The content of carbohydrates, proteins and lipids of some marine algae

Marine algae	Carbohydrates, % (w/w)	Proteins, % (w/w)	Lipids, % (w/w)	References
Green marine algae				
Ulva lactuca	59.0	17.0	3–4	Jambo et al. (2016)
Cladophora rupestris		3.4	0.6	Maehre et al. (2014)
Ulva intestinalis		11.3	1.1	Maehre et al. (2014)
Red marine algae				
Gelidium amansii	66.0	20.0	0.2	Jambo et al. (2016)
Gracilaria verrucosa	60.8	9.9	0.8	Meinita et al. (2017)
Palmaria palmata	39.4	22.9	3.3	Kostas et al. (2016)
Chondrus crispus	21.8	19.9	0.5	Kostas et al. (2016)
Brown marine algae				
Fucus serratus	26.4	9.6	2.8	Kostas et al. (2016)
Laminaria digitata	21.7	26.8	1.9	Kostas et al. (2016)
Laminaria japonica	51.0	8.0	1.0	Jambo et al. (2016)
Undaria pinnatifida	43.0	24.0	3–4	Jambo et al. (2016)

micrometers (microscopic unicellular algae) to a few tens of meters (macroscopic multicellular algae).

Mostly, seaweeds are classified according to the colour of the pigments in their composition (Davis et al. 2003; Guiry 2012). The mixture of pigments in their chloroplasts lends characteristic colours, and thus the marine algae can be divided in three categories:

- Green algae – Chlorophyta division
- Red algae – Rhodophyta division
- Brown algae – Phaeophyta division

In addition to colour pigments, marine algae also have, in their composition, carbohydrates, proteins and lipids, whose types and concentrations differ from one category to another. Table 4.3 shows the content of each of these component classes for some marine algae. Thus, the cell walls of green algae mainly contain cellulose and proteins bonded to polysaccharides (Romera et al. 2007; Wang et al. 2009). The red algae have in their composition cellulose (as structural support polysaccharide), agar and carraghenates (Romera et al. 2006; Romera et al. 2007). The brown algae generally contain cellulose (i.e., the structural support), alginic acid and sulphated polysaccharides (Lodeiro et al. 2005; Romera et al. 2007).

Differences in the composition of marine algae determine a different structure of cell walls, which is one of the main factors influencing the ability of marine algae to uptake heavy metal ions from aqueous media. This is because the constituents of marine algae cell walls have different functional groups (such as hydroxyl, carboxyl, carbonyl, amino, sulphate, etc.) that can interact with heavy metal ions from aqueous media (often trough ion exchange) and thus will play an important role in the biosorption processes.

The nature of the functional groups in the marine algae structure can be easily identified from the FTIR spectra recorded for dry biomass. The absorption bands from FTIR spectra can be assigned to various functional groups in function of the maximum absorption wave numbers and using the correlation tables. Figure 4.1 shows the FTIR spectrum of *Ulva lactuca* marine algae and illustrates the main functional groups identified in this spectrum.

Such functional groups have been identified in the FTIR spectra of all categories of marine algae (Donmez et al. 1999; Davis et al. 2003; Lesmana et al. 2009; Romera et al. 2007; Wang et al. 2009) and have been considered to be the binding sites for the heavy metal ions from aqueous solution. But, in the structure of marine algae cell walls, these functional groups are not in free forms. The high concentration of Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}, ions in seawater (which is the natural growth medium), makes that these ions bound to these functional groups. The high content of alkaline and alkaline earth metal ions in the composition of marine algae (Table 4.4) is another advantage from biosorption perspective, because these cations will be easily replaced by the heavy metal ions through a simple ion-exchange process.

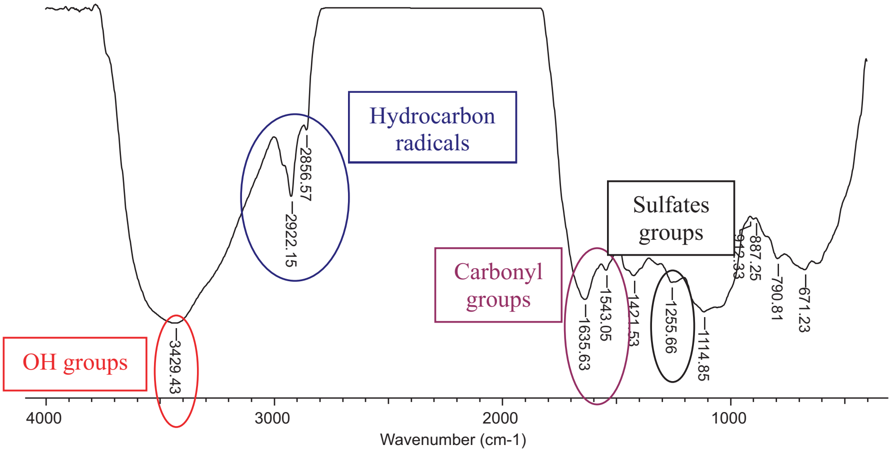

Fig. 4.1 FTIR spectrum of *Ulva lactuca* marine algae. (Adapted after Lupea et al. 2012a)

Table 4.4 The content of alkaline and alkaline earth metal ions of some marine algae (Simionescu et al. 1974)

Marine algae		Na, mg/g	K, mg/g	Ca, mg/g	Mg, mg/g
Brown algae	*Fucus visoides*	173.05	42.71	20.03	12.11
	Cystoseira barbata	145.0	86.61	27.31	10.0
Red algae	*Gracilaria compressa*	49.01	50.81	33.12	7.75
	Gracilaria confervoides	32.75	0.18	30.51	4.34
Green algae	*Ulva lactuca*	43.17	23.14	31.80	18.91

Many studies from literature have shown that the brown marine algae have the higher ion-exchange capacity compared with red or green marine algae (Romera et al. 2007; Chojnacka 2010; Mazur et al. 2018). This characteristic is mainly due to the high content of alginate (10–40%) and fucoidan (5–20%) in their structure (Michalak et al. 2013) which determines the presence of a higher number of functional groups on their surface.

Unfortunately, the use of brown and red marine algae in the biosorption processes of heavy metal ions has an important drawback, which drastically limits their industrial applications. Thus, during biosorption, certain organic compounds from marine algae composition (such as alginate, colour pigments, etc.) can be released into the aqueous media, generating the secondary pollution of the treated effluent and the decrease of marine algae biosorption capacity (Yang and Chen 2008).

Unlike these, in marine green algae, the leaching of organic compounds is insignificant, and therefore the effect of secondary pollution is missing most of the time, but also their biosorption capacity is lower compared with brown and red marine algae (Tobin et al. 1988; Hamdy 2000; Apiratikul and Pavasant 2008). Considering all the aspects discussed in this section, it can be said that in the preparation of marine algae as biosorbents for the removal of toxic heavy metal ions from aqueous media, only a few simple steps are required. Figure 4.2 illustrates the main elementary steps involved in the preparation of marine algae biosorbents.

The harvested marine algae are immediately washed with demineralized water to remove the dissolved salts from their leaves. Otherwise, the dissolved salts will significantly change the ionic strength of the aqueous solutions, and their presence will affect the efficiency of the biosorption process. After washing, the drying of marine algae is done in air, often at ambient temperature, because in this way, the humidity is gradually removed and the surface of the algae particles will be wrinkled and cracked more, which will provide a larger specific surface area. The last

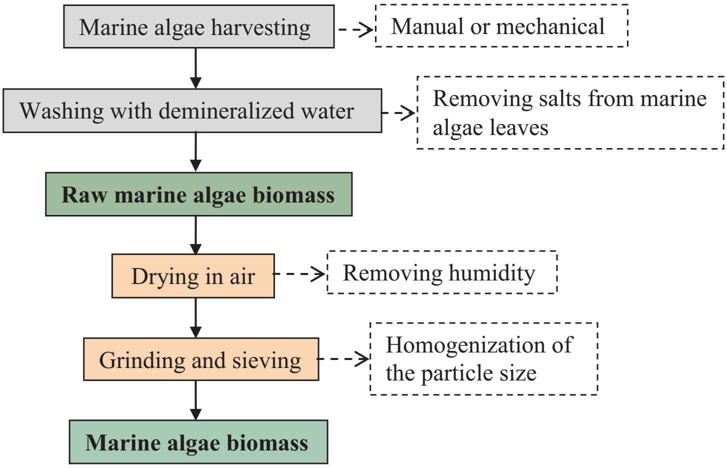

Fig. 4.2 The main steps in the preparation of marine algae biosorbents

important step in the preparation of marine algae biomass is grinding and sieving, which will provide almost the same size of biomass particles.

Under these conditions, the marine algae can be considered "low-cost" biosorbents, which require a few simple steps of preparation and which due to numerous and varied functional groups can be used to design effective biosorption systems to remove toxic heavy metals from aqueous effluents.

4.4 Marine Algae Biosorbents for Removal of Toxic Heavy Metals

As shown in the previous paragraph, the marine algae biomasses have in their composition different organic compounds (such as carbohydrates, proteins, lipids, etc.) that possess numerous and varied functional groups. These functional groups represent the binding sites for toxic heavy metal ions during of biosorption. Under these conditions, the efficiency of biosorption processes will mainly depend on the efficiency of functional groups – heavy metal ion interactions – and this will be affected by:

- The dissociation degree of functional groups
- The speciation form of toxic heavy metal ions
- The number of binding sites form biomass surface
- The contact time between marine algae biomass (solid) and heavy metal ions (aqueous solution)
- Temperature

All these factors will define the experimental conditions in which the biosorption process is carried out, and hence the finding of optimal experimental conditions will ensure the maximum efficiency of the biosorption process. Only when the optimal experimental conditions have been selected (on the basis of experimental and/or computational studies), the biosorption process can be assessed and can be determined by the biosorptive performance of marine algae biomass for a given metal ion.

4.4.1 Selection of Optimal Conditions for the Biosorption Process

It is well known that the retention of metal ions from aqueous media by biosorption using marine algae biosorbents takes place with maximum efficiency only in certain experimental conditions (Donmez et al. 1999; Febrianto et al. 2009; Robals et al. 2016). The most important experimental parameters to be considered when determining the optimal conditions for the biosorption process are:

(i) *Initial solution pH* – because its value depends on the speciation form of toxic heavy metal ions in aqueous solution and the dissociation degree of functional groups from marine algae biomass surface.

(ii) *Biomass dosage* – the amount of marine algae biomass used to remove toxic heavy metal ions from a given volume of aqueous solution determines the number of active sites that may be involved in the biosorption process, and the value of this parameter is important both from economical and technological considerations.
(iii) *Contact time* – an optimal value of this parameter indicates the minimum time required to achieve the interactions between heavy metal ions and superficial functional groups of marine algae biomass and plays an important role in the kinetics modelling of biosorption process.
(iv) *Temperature* – the finding of optimal value of this parameter is important both theoretical considerations, as it allow for the thermodynamic modelling of the biosorption processes, as well as for applicative considerations, because its value can significantly influence the cost of biosorption processes.

Even if in literature the initial heavy metal concentration is considered another experimental parameter that affects the efficiency of biosorption process, its influence is more theoretically important for the modelling of biosorption processes than from a practical point of view because it is well known that in the case of industrial effluents, the concentration of the heavy metal ions varies in a fairly narrow range and their composition is complex.

The effect of each of these experimental parameters on the biosorption efficiency must be analyzed one by one, and the obtained results will allow the selection of the optimal conditions for that the biosorption process takes place with maximum efficiency for a certain toxic heavy metal ion and a certain marine algae biosorbent. Several examples of optimal experimental conditions established for the biosorption of various heavy metal ions on different marine algae biosorbents are summarized in Table 4.5.

Initial solution pH is one of the most important experimental parameters that affects the efficiency of biosorption processes, because its value determined not only the dissociation degree of functional groups from marine algae biomass surface but also the speciation and availability of heavy metal ions to participate at biosorption process (Marques et al. 2000; Esposito et al. 2002). As can be seen from Table 4.5, most of biosorption processes of heavy metal ions on marine algae biosorbents take places with a maximum efficiency at an initial solution pH between 4.0 and 6.0. Obtaining the maximum efficiency of biosorption processes in such a narrow pH range can be explained on the basis of the following considerations:

- *At low pH* (pH < 4.0) – even if most heavy metal ions are predominantly as free as positively charged cations (M^{n+}) in aqueous solution, functional groups in the surface area of marine algae biomass are largely non-dissociated or positively charged, which makes chemical interactions not happen due to the electrostatic repulsive forces. Only the metal ions which exist in the solution as negatively charged species (oxo-anions) can be retained by the marine algae biomass at a very low initial solution pH (Murphy et al. 2008). It is the case of Cr(VI) ions biosorption, for which the optimal pH value is obtained in the pH range of 0.5–1.5 (see Table 4.5), regardless of the type of marine algae biosorbent.

Table 4.5 The experimental conditions selected as optimal for the removal of heavy metal ions by biosorption on marine algae biomass

Metal ion	Marine algae biomass		Optimal experimental conditions for biosorption				References
			pH	Dosage, g/L	t, min	Temperature, °C	
Cu(II)	Green algae	*Ulva fasciata*	5.5	1.0	30	22	Karthikeyan et al. (2007) and Kumar et al. (2006)
		Chaetomorpha linum	5.0	2.0	120	23	Ajjabi and Chouba (2009)
		Spirogyra spp.	5.0	1.0	30	Ambient temp.	Lee and Chang (2011)
	Red algae	*Asparagopsis armata*	5.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Chondrus crispus	4.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Ceramium rubrum	6.0	4.0	90	35	Egel and Doner 2013
	Brown algae	*Fucus vesiculosus*	5.0	1.0	120	23	Mata et al. (2008)
		Sargassum sp.	5.5	1.0	30	25	Karthikeyan et al. (2007)
		Fucus spiralis	5.0	0.5	120	Ambient temp.	Romera et al. (2007)
	Green algae	*Ulva lactuca*	5.0	0.1	60	20	Sari and Tuzen (2008a) and Lupea et al. (2012a)
		Chlorophyta sp.	4.0	4.0	30	25	Sulaymon et al. 2013
		Caulerpa fastigiata	5.5	10.0	60	25	Sarada et al. 2014
	Red algae	*Ceramium virgatum*	5.0	0.1	60	20	Sari and Tuzen (2008b)
		Kappaphycus alvarezii	4.5	2.0	45	32	Praveena and Vijayaraghavan (2015)
		Corallina mediterranea	5.0	10.0	60	25	Ibrahim (2011)
	Brown algae	*Fucus serratus*	4.5	2.5	25	25	Herrero et al. (2006)
		Saccorhiza polyschides	4.5	2.5	> 60	25	Lee and Chang (2011)
		Cystoseira baccata	4.5	2.5	17	25	Lodeiro et al. (2006)
Cr(VI)	Green algae	*Ulva lactuca*	1.0–1.5	3.0	120	25	El-Sikaily et al. (2007)
		Ulva compressa	2.0	2.0	120	Ambient temp.	Murphy et al. (2008)
		Cladophora albida	2.0	4.0	30	25	Deng et al. (2009)
	Red algae	*Palmaria palmate*	2.0	2.0	30	Ambient temp.	Murphy et al. (2008)
		Polysiphonia lanosa	2.0	2.0	30	Ambient temp.	Murphy et al. (2008)
		Ceramium virgatum	1.5	0.1	90	20	Sari and Tuzen (2008c)
	Brown algae	*Fucus vesiculosus*	2.0	2.0	120	Ambient temp.	Murphy et al. (2008)
		Fucus spiralis	2.0	2.0	120	Ambient temp.	Murphy et al. (2008)

(continued)

Table 4.5 (continued)

Metal ion	Marine algae biomass		Optimal experimental conditions for biosorption				References
			pH	Dosage, g/L	t, min	Temperature, °C	
Ni(II)	Green algae	*Ulva lactuca*	4.5	2.0	60	30	Zakhama et al. (2011)
		Cladophora spp.	5.0	5.0	–	23	Zakhama et al. (2011)
		Codium vermilara	6.0	0.5	120	Ambient temp.	Romera et al. (2007)
	Red algae	*Asparagopsis armata*	6.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Chondrus crispus	6.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Kappaphycus alvarezii	4.5	2.0	45	32	Praveena and Vijayaraghavan (2015)
	Brown algae	*Padina australis*	6.0	1.0	120	30	Kalyani et al. (2004)
		Fucus spiralis	6.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Ascophyllum nodosum	6.0	0.5	120	Ambient temp.	Romera et al. (2007)
Pb(II)	Green algae	*Ulva lactuca*	5.0	8.0	30	22	Bulgariu et al. (2010)
		Cladophora fasci.	5.0	2.0	30	25	Deng et al. (2007)
		Spirogyra spp.	5.0	0.5	100	20	Lee and Chang (2011)
	Red algae	*Asparagopsis armata*	4.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Chondrus crispus	4.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Kappaphycus alvarezii	4.5	2.0	45	32	Praveena and Vijayaraghavan 2015
	Brown algae	*Fucus spiralis*	5.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Ascophyllum nodosum	5.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Fucus vesiculosus	5.0	1.0	120	23	Mata et al. (2008)
Zn(II)	Green algae	*Spirogyra insignis*	6.0	1.0	120	Ambient temp.	Romera et al. (2007)
		Chaetomorpha linum	5.0	20	120	25	Ajjabi and Chouba (2009)
		Ulva fasciata sp.	5.0	0.1	20	30	Kumar et al. (2007)
	Red algae	*Asparagopsis armata*	6.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Chondrus crispus	6.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Gracilaria caudata	5.0	1.5	120	25	Cechinel et al. (2018)
	Brown algae	*Fucus spiralis*	6.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Ascophyllum nodosum	6.0	0.5	120	Ambient temp.	Romera et al. (2007)
		Laminaria hyperborea	5.0	2.0	45	25	Freitas et al. (2008)

- *At higher pH values* (pH > 6.0) – the functional groups from marine algae biomass surface have a high dissociation degree (most of them becoming negatively charged), but the biosorption process can be prevented by changing the speciation form of heavy metal ions from aqueous solution. This is because at high initial solution pH, the hydrolysis of metal ions can take place and the formed hydrolyzed metallic species no longer have the same availability for biosorption processes (Romera et al. 2007).

The decreasing of the biosorption efficiency at initial solution pH lower than 4.0 and higher than 6.0 can be easily observed in case of some toxic heavy metal ion retention on *Ulva lactuca* marine green algae biomass (Fig. 4.3).

Therefore, choosing an initial solution pH between 4.0 and 6.0 (see Table 4.5) will ensure both a dissociation degree of functional groups of marine algae biomass sufficiently high and an adequate speciation form of the toxic heavy metal ions so that the biosorption process occurs with maximum efficiency.

The quantity of marine algae biomass used as biosorbent for a given volume of aqueous solution with known concentration of toxic heavy metal ions may also influence the efficiency of biosorption processes. For the selection of the optimal biosorbent dosage, it is necessary to analyze the performances of biosorption process, as well as some economic and operational aspects. In the analysis of the biosorption process performances, studies from literature (Gokhale et al. 2008; Farooq et al. 2010; Finocchio et al. 2010) have shown that:

- The removal percent of toxic heavy metal ions from aqueous solution increases with the increasing of marine algae biomass dose, mainly due to the increase of the number of active sites (superficial functional groups) which can bond metal ions from aqueous solution.

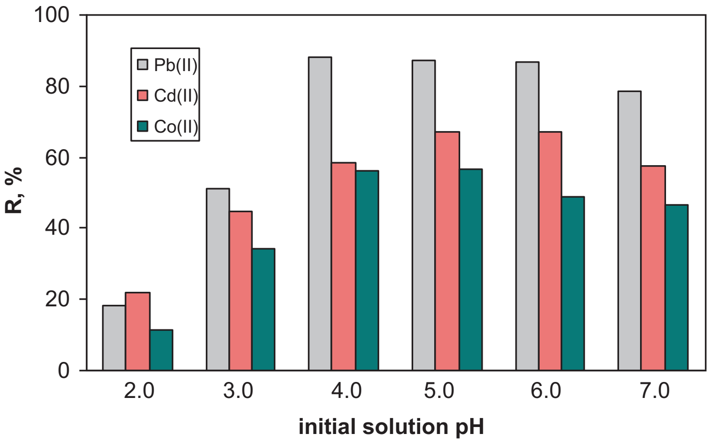

Fig. 4.3 Variation of the biosorption efficiency in function of initial solution pH in case of *Ulva lactuca* marine green algae biomass. (Bulgariu and Bulgariu 2012; Lupea et al. 2012a, b)

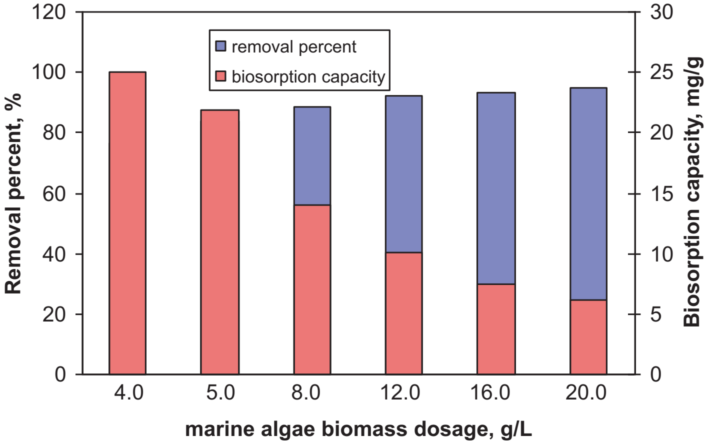

Fig. 4.4 Variation of the biosorption process parameters as a function of biosorbent dosage in case of Pb(II) biosorption on *Callithamnion corymbosum* algae biomass

- The biosorption capacity of marine algae biomass decreases with the increasing of biosorbent dosage due to the fact that the metal ions have more functional groups available for interaction, and this makes the amount of metal ions retained per weight unit of marine algae biomass (which means the biosorption capacity) to decrease.

A suggestive illustration of such opposite variation of these two parameters (biosorption capacity and percent removal) is presented in Fig. 4.4, for the biosorption of Pb(II) ions from aqueous media on *Callithamnion corymbosum* algae biomass (red marine algae).

Therefore, in most of cases, the biosorption of toxic heavy metals requires relatively low quantities of marine algae biomass (see Table 4.5), which will allow for high biosorption performance of marine algae biomass (high values of biosorption capacity) but also a high efficiency of biosorption process (high values of removal percent).

On the other hand, the use of low amounts of marine algae biosorbents in the biosorption processes of toxic heavy metal ions also has several economic and operating advantages, because:

- The low amounts of marine algae biosorbent used in the biosorption processes will reduce the costs and generate low amounts of waste biomass loaded with toxic heavy metal ions, which have been also properly treated so as not to become a danger to the environment.
- Some technological operations, such as mixing, filtration, transport, etc., will require low time and energy consumption.

Biosorption of toxic heavy metals depends largely on contact time. The studies from literature that discuss the kinetics of toxic heavy metal ion biosorption on

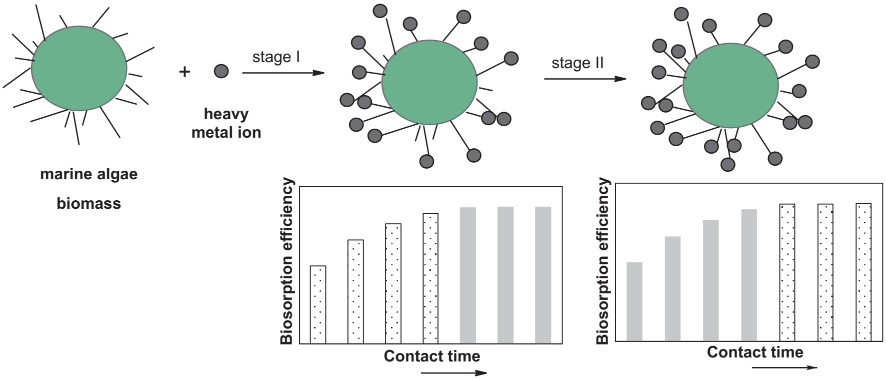

Fig. 4.5 Dependence between the biosorption efficiency and contact time in case of marine algae biosorbents

marine algae biomass (Sheng et al. 2004; Lee and Chang 2011; Zeraatkar et al. 2016) indicate that the biosorption process generally takes place in two stages:

- *Stage I* – rapid stage – in the first 5–30 min, the amount of heavy metal retained on marine algae biomass surface increases sharply, and the values of removal percents can attain 90% from initial concentration of heavy metal ion.
- *Stage II* – slower stage – can take up to 3–4 h, and where the amount of heavy metal ions retained on marine algae biomass surface does not vary by more than 5–10%.

Figure 4.5 presented a typical variation of the biosorption efficiency of toxic heavy metal ions on marine algae biomass in function of contact time.

Such two-step biosorption process of toxic heavy metal ions on marine algae biomass can be explained as (Qin et al. 2006; Gerente et al. 2007; Febrianto et al. 2009):

- *In stage I* – all superficial functional groups of marine algae biomass are free and geometrical available for to interact with heavy metal ions from aqueous solution. Therefore, the electrostatic interactions can easily occur, and the ion-exchange processes are effective in the binding of heavy metal ions on the surface of marine algae biomass.
- *In stage II* – majority of superficial functional groups are already occupied, and the heavy metal ions should find the superficial groups within the pores of marine algae biomass particle to interact. In this case, the elementary diffusion process became the rate-limiting step, and the efficiency of biosorption process does not vary significantly.

The fast biosorption of toxic heavy metal ions on marine algae biomass (see Table 4.5) has very important practical and economical consequences, because it allows the scale-up of the biosorption process on industrial scale, which will ensure high efficiency and low cost of operating (Liu et al. 2009).

Temperature can influence the efficiency of toxic heavy metal ion biosorption on marine algae biomass but to a much lower extent than the other experimental parameters mentioned above. This is because the rise of temperature must be done only up to 50–60 °C, in order to prevent the degradation of marine algae biomass, and under these conditions, the variation of the biosorption capacity is most often quite small for the biosorption of most heavy metal ions (Monteiro et al. 2010; Johansson et al. 2016). But, in function of the nature of marine algae biomass used as biosorbent and the type of toxic heavy metal from aqueous solution, the increase of temperature can determine:

- *The increase of the biosorption capacity* – which means that the biosorption process is of endothermic nature (Gupta and Rastogi 2008; Romera et al. 2007; Johansson et al. 2016)
- *The decrease of the biosorption capacity* – indicating an exothermic nature of the biosorption process (Cruz et al. 2004; Sari and Tuzen 2008a)
- *Insignificant changes of the biosorption capacity* (Martins et al. 2004; Lodeiro et al. 2006; Lupea et al. 2012a)

However, by comparing the variation in biosorption capacities and the costs required for temperature rise, in most cases the ambient temperature is considered to be optimal (see Table 4.5), especially for economic reasons (Wang and Chan 2009).

4.4.2 Biosorptive Performances of Marine Algae Biosorbents

The retention of toxic heavy metal ions on marine algae biomass through biosorption is a non-metabolically process, in which the metal ions are bonded on marine algae surface by ion-exchange, superficial complexation, adsorption, coordination, or micro-precipitation (Febrianto et al. 2009). Therefore, the biosorption can be considered a physicochemical process, whose efficiency is mainly dictated by the elementary interactions between functional groups of marine algae biosorbents and toxic heavy metal ions from aqueous media.

As it was already mentioned in the previous paragraphs, the constituents of marine algae biomass provide various functional groups (such as hydroxyl, carboxyl, carbonyl, sulphonic, etc.), which represent the binding sites and which determine the retention of toxic heavy metal ions from aqueous media, through specific interactions. In optimal experimental conditions (pH and biosorbent dosage), most of these functional groups are dissociated and will generate negative charges on the marine algae biomass surface. These negative charges are responsible for the electrostatic interactions with metal ions from aqueous solution (Murphy et al. 2008; Mazur et al. 2018). Therefore, the toxic heavy metal ions will be retained by marine algae biomass, and most of the studies from literature indicate that such biosorption process occurs until to the formation of complete monolayer coverage, according with Langmuir isotherm model (Chong and Volesky 1995; Rangabhashiyam et al. 2014). The number and availability of functional groups from marine algae biomass surface will dictate the efficiency of the biosorption process in selected optimal experimental conditions, and the parameter used for the quantitative evaluation of this efficiency is the maximum biosorption capacity (q_{max}, mg/g). The maximum biosorption capacity indicates the maximum amount of toxic heavy metal ions retained on weight unit of marine algae biomass and may be calculated from linear Langmuir equation (Rangabhashiyam et al. 2014).

On the other hand, the toxic heavy metal ions from aqueous solution have different affinities for the functional groups of marine algae biomass. In the optimal experimental conditions (pH, contact time) selected so that such interactions to be facilitated, the heavy metal ions will be retained on marine algae biomass the easier as their affinity for the functional groups present on the biosorbent surface will be greater. The ease with which metal ions interact with functional groups of marine algae biomass may be evaluated by kinetics modelling of the biosorption process, and the quantitative parameter used in this case is constant rate (which represents the amount of toxic heavy metal ions retained on mass unit of biosorbent in time unit).

Most of the biosorption processes which use marine algae biosorbents follows a pseudo-second order kinetics model, and under these conditions, the rate constant is calculated from the linear pseudo-second-order kinetics equation (Febrianto et al. 2009; Ibrahim 2011). This means that for the retention of a heavy metal ion, two binding sites are required (Chojnacka 2010), and therefore beside the number, the geometrical availability of functional groups from marine algae biomass surface will significantly affect the performances of the biosorption processes.

Starting from these observations, always in assessing the performance of biosorption processes should be considered the values of maximum biosorption capacity (which is a measure of the availability of marine algae biomass to participate at the biosorption processes) and of kinetics constant rate (which indicate the affinity of metal ions from aqueous solution to interact with the functional groups of biosorbent). Several examples in this regard are shown in Table 4.6.

The values presented in Table 4.6 show that, in most of cases, the brown marine algae biomass showed higher biosorptive performances in the removal processes of different toxic heavy metal ions, compared with red or green marine algae biomass. The high biosorption capacity of brown marine algae biomass has been attributed to the presence of high concentration of alginate in their cell walls, which is mainly responsible by such high toxic metal ions removal ability (Mazur et al. 2018). Thus, Romera et al. (2007) have shown that the affinity of toxic heavy metal ions to alginate (or fucoidan) depends by their geometrical radius and follows the order: Pb(II) > Cu(II) > Cd(II) > Zn(II) > Ni(II). This increasing of the biosorption capacity of marine brown algae with the increasing of metal ion radius is a consequence of stereochemical effect, because the metal ions with larger volume can find easier binding site with two distant functional groups, on marine algae surface. Unfortunately, the use of brown marine algae biomass in the biosorption processes of heavy metal ions can cause the contamination of treated aqueous effluent with organic compounds which are released from their composition, during of biosorption. This negative effect of secondary pollution is also undesirable and can be

Table 4.6 Biosorptive performances of different types of marine algae biomass for different toxic heavy metal ions in the biosorption processes

Metal ion	Marine algae biomass		Biosorptive performances		References
			q_{max}, mg/g	k, g/mg min	
Cu(II)	Green algae	*Ulva fasciata* sp.	73.50	0.013	Karthikeyan et al. (2007)
		Spirogyra sp.	38.61	–	Lee and Chang (2011)
		Cladophora sp.	14.71	–	
	Red algae	*Osmundea pinnatifida*	6.94		El Hassouni et al. (2014)
		Gymnogongrus torulosus	51.47	0.019	Areco and dos Santos Afonso (2010)
		Pterocladia capillacea	49.50	0.042	El-Sikaily et al. (2011)
	Brown algae	*Fucus serratus*	101.73	0.051	Ahmady-Asbchin et al. (2008) and Mata et al. (2008)
		Undaria pinnatifida	78.88	4.84	Chen et al. (2008)
		Laminaria sp.	61.59	0.024	Liu et al. (2009) and Freitas et al. (2008)
Cd(II)	Green algae	*Oedogonium* sp.	88.20	0.012	Gupta and Rastogi (2008)
		Ulva lactuca	41.66	0.011	Lupea et al. (2012a)
		Chaetomorpha linum	53.96	0.034	Hashim and Chu (2004)
	Red algae	*Gelidium*	18.02	0.086	Vilar et al. (2006)
		Ceramium virgatum	39.70	0.003	Sarı and Tuzen (2008b)
		Gracilaria edulis	26.98	0.026	Hashim and Chu (2004)
	Brown algae	*Laminaria* sp.	104.53	0.024	Delle (2001) and Freitas et al. (2008)
		Cystoseira baccata	77.56	0.007	Lodeiro et al. (2006)
		Undaria pinnatifida	121.40	0.002	Plaza Cazón et al. (2013)
Cr(VI)	Green algae	*Caulerpa racemosa*	0.57	0.011	Pandya et al. (2017)
		Ulva lactuca	55.55	0.024	
		Oedogonium sp.	35.41	0.212	Bakatula et al. (2014)
	Red algae	*Ceramium virgatum*	26.50	0.024	Sarı and Tuzen (2008c)
		Palmaria palmate	33.80	–	Murphy et al. (2008)
		Polysiphonia lanosa	45.76	–	
	Brown algae	*Fucus vesiculosus*	42.64	–	
		Fucus spiralis	35.36	–	
		Bifurcation bifurcata	23.40	1.666	Ainane et al. (2014)

Ni(II)	Green algae	*Oedogonium* sp.	26.18	0.042	Bakatula et al. (2014)
		Ulva sp.	12.91	0.015	Sheng et al. (2004)
	Red algae	*Gracilaria caudata*	50.10	0.066	Bermudez et al. (2011)
		Gracilaria sp.	16.10	0.011	Sheng et al. (2004)
	Brown algae	*Laminaria* sp.	66.33	0.167	Liu et al. (2009)
		Sargassum glaucescens	52.63	0.102	Pahlavanzadeh et al. (2010)
		Cystoseira indica	47.62	0.022	Pahlavanzadeh et al. (2010)
Pb(II)	Green algae	*Cladophora* sp.	200.42	0.012	Deng et al. (2007)
		Oedogonium sp.	144.92	0.064	Gupta and Rastogi (2008)
		Caulerpa fastigiata	17.51	0.083	Sarada et al. (2014)
	Red algae	*Gymnogongrus torulosus*	140.89	0.011	Areco and dos Santos Afonso (2010)
		Jania rubens	30.6	0.012	Ibrahim (2011)
		Pterocladiella capillacea	34.1	0.011	
	Brown algae	*Lobophora* sp.	580.16	–	Jha et al. (2009)
		Cystoseira baccata	182.33	0.001	Lodeiro et al. (2006)
		Laminaria japonica	213.42	0.020	Luo et al. (2006) and Freitas et al. (2008)
Zn(II)	Green algae	*Ulva fasciata* sp.	13.50	0.168	Kumar et al. (2007)
		Ulva lactuca	31.05	0.092	Badescu et al. (2017)
		Oedogonium sp.	36.55	0.038	Bakatula et al. (2014)
	Red algae	*Gymnogongrus torulosus*	44.46	0.022	Areco and dos Santos Afonso (2010)
		Gracilaria sp.	26.15	0.023	Sheng et al. (2004)
		Jania rubens	25.81	0.021	Ibrahim (2011)
	Brown algae	*Laminaria* sp.	54.26	0.075	Freitas et al. (2008)
		Sargassum muticum	49.63	0.012	Freitas et al. (2008)
		Undaria pinnatifida	10.46	0.024	Plaza Cazón et al. (2013)

minimized by a preliminary treatment of brown marine algae biomass with dilute solutions of alkali.

In case of red algae, the sulphated polysaccharides (galactanes) were found to be mainly responsible for the retention of toxic heavy metal ions from aqueous solution, often by electrostatic interactions (ion exchange or superficial complexation) (Romera et al. 2007). This kind of algae will prefer to retain toxic heavy metal ions with high affinity for O-donor groups, such as Pb(II), Cu(II), or Ni(II) (see Table 4.6). And in case of red marine algae biosorbents, the secondary pollution can be observed, but its intensity is lower compared with brown marine algae biomass, and can be minimized in the same way.

The green algae have in their composition numerous carboxyl, hydroxyl, sulphate, phosphate and amine groups from α-, β- and γ-carotenes and several xanthophylls (Gupta and Rastogi 2008) and will bind the heavy metal ions from aqueous solution, predominantly through ion-exchange interactions. This kind of interactions is not selective, and therefore the biosorption capacity of green marine algae are significantly influenced by the presence of other metal ions in aqueous solution (Hashim and Chu 2004; Gupta and Rastogi 2008; Pandya et al. 2017). However, it should be noted that in case of marine green algae biomass, the intensity of the secondary pollution effects is much lower compared with red and brown marine algae biomasses and that due to the high number of amino groups from their structure have the best performances in the retention of Cr(VI) ions, if the experimental conditions are adequate (see Table 4.6).

4.5 Regeneration and Recycling of Exhausted Marine Algae Biomass

The evaluation of the biosorptive performances of marine algae biomass in the removal processes of toxic heavy metal ions from aqueous effluents is not complete without the studies related to the regeneration and recycling of exhausted biosorbents. This is because the possibility to use the same quantity of marine algae biomass in multiple biosorption processes offers important environment and economic benefits. The chemical process involved in this case is named desorption, and suppose the mixing of exhausted marine algae biomass with a desorption agent, in certain experimental conditions (contact time, exactly known volume and concentration of desorption agent, temperature, etc.), when the retained toxic heavy metal ions are replaced by other ions of desorption agent structure (Lasheen et al. 2012; Robalds et al. 2016; Kolodynska et al. 2017). The elementary processes that occur in desorption of toxic heavy metal ions from exhausted marine algae biomass are mainly ion-exchange type (Fig. 4.6), and suppose the release of retained toxic heavy metal ions in aqueous solution concomitant with the regeneration of marine algae biomass. Because the released toxic metal ions can be recovered and reintroduced in the industrial activities and that the regenerated biosorbent can be used in another

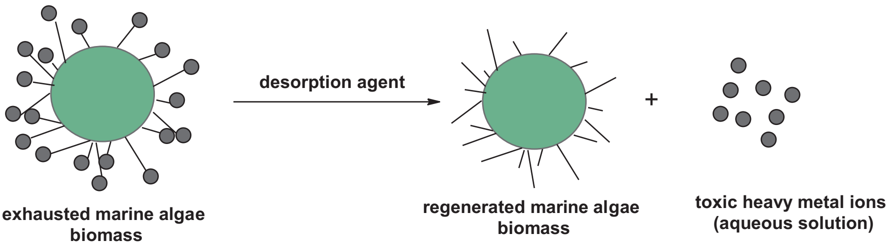

Fig. 4.6 Schematic illustration of the toxic heavy metal ions desorption from exhausted marine algae biomass

biosorption cycle, desorption will contribute to lowering the costs of removing toxic heavy metal ions from aqueous media.

The quantitative desorption of the toxic heavy metal ions retained on marine algae biomass and the regeneration of biosorbents can be done using various chemical reagents, such as mineral acids (HCl, HNO_3, etc.), inorganic salts (NaCl, $NaNO_3$, KNO_3, $CaCl_2$, etc.), or complexing agents (EDTA), in various experimental conditions (Gupta et al. 2015; De Gisi et al. 2016; Tran and Chao 2018). After desorption, the aqueous solution contains the toxic heavy metal ions, which can be recovered through specific procedures, and the solid phase is the regenerated marine algae biosorbent, which is washed, dried and conditioned, in order to be used in another biosorption cycle (Kolodynska et al. 2017). However, for desorption processes to be effective, the following should be considered:

- The solution of desorption agent should have a pH with a least 2–4 units lower than the optimal pH used for the biosorption of heavy metal ions.
- The ratio between the exhausted marine algae biomass and the volume of desorbent solution should be high, so that a low volume of desorbent solution is used to treat the large amount of depleted biosorbent – in this way the costs related to biosorbent regeneration and recovery from the released heavy metal is minimized.
- The concentration of the desorbent solution must be high (10^{-3} – 1.0 mol/l) so that the desorption process is efficient.
- The desorption processes should take place at ambient temperature and only when it is absolutely necessary at higher temperatures – in this way the cost of desorption processes is kept low, and the damage of the regenerated marine algae biosorbents is avoided.

In Table 4.7 are presented several desorption possibilities of toxic heavy metal ions form exhausted marine algae biomass that can be used for the recovery of metal ions and biosorbent regeneration.

Most often, mineral acids such as HCl or HNO_3 are used for the desorption of toxic heavy metal ions from exhausted marine algae biomass (Gupta et al. 2015; Tran and Chao 2018), because they (i) have high efficiency in desorption processes (95–97%) compared with inorganic salts (see Table 4.7) and (ii) facilitate the

Table 4.7 Characteristics of some desorption processes used for the treatment of exhausted marine algae biomass loaded with toxic heavy metal ions

Metal ion	Marine algae biomass	Desorption agent	Metal recovery, %	References
Cd(II)	*Ulva lactuca*	0.1 M HCl	> 98	Lupea et al. (2012a)
	Oedogonium sp.	0.5 M HCl	84.80	Gupta and Rastogi (2008)
Cu(II)	*Halimeda gracilis*	0.2 M HCl	88.13	Jayakumar et al. (2015)
Cr(VI)	*Halimeda gracilis*	0.2 M HCl	98.02	Jayakumar et al. (2014)
Pb(II)	*Sargassum* sp.	0.1 M HNO_3	> 95	Martins et al. (2006)
Zn(II)	*Scenedesmus* sp.	0.1 M H_2SO_4	98.40	Sarwa and Verma (2014)
	Fucus vesiculosus	1 N HNO_3	≈ 100	Castro et al. (2017)
Cu(II)	*Gracilaria caudata*	0.5 M $CaCl_2$	38.00	Cechinel et al. (2018)
		0.5 M NaCl	90.00	
Ni(II)	*Gracilaria caudata*	0.5 M $CaCl_2$	58.00	
		0.5 M NaCl	52.00	
Zn(II)	*Gracilaria caudata*	0.5 M $CaCl_2$	100	
		0.5 M NaCl	59.00	
	Ulva lactuca	0.1 M NaCl	78.60	Badescu et al. (2017)
		0.1 M $CaCl_2$	92.00	
Pb(II)	*Sargassum* sp.	0.1 M EDTA	95.00	Martins et al. (2006)

recovery of the desorbed metal ions, which are found in aqueous solution as simple chemical species, compared with complexing agents (when the desorbed metal ions are released in aqueous solution as complex species, which make their recovery to be more difficult) (Martins et al. 2006).

However, the efficiency of the regenerated marine algae biomass in the biosorption processes of toxic heavy metal ions decreases as the number of biosorption/desorption cycles increases (Gautam et al. 2015; Cechinel et al. 2018; Tran and Chao 2018). This makes that in most cases, the use of marine algae biomass is not efficient after 6–8 repeated use (Table 4.8).

The loss in the biosorption efficiency of regenerated marine algae biomass in superior cycles is probably caused by (Gautam et al. 2015; Zeraatkar et al. 2016):

- Incomplete desorption of toxic heavy metal ions – if the desorption agent is not suitable or he does not have a well-chosen concentration, not all the toxic metal ions retained by biosorption are released in the desorption processes, and so some functional groups from marine algae biomass surface are not released after desorption.
- After several treatments of exhausted marine algae biomass with concentrated solution desorption agents, the structure of biomass can be irreversibly degraded, due to the low mechanical resistance of marine algae biomass that results in a decrease in the number of functional groups available for toxic heavy metal biosorption.

Table 4.8 Decreasing of biosorption efficiency (% loss) of marine algae biomass in multiple biosorption/desorption cycles of toxic heavy metal ions

Metal ion	Marine algae biomass	Desorption agent	No. cycles	% loss	References
Cd(II)	*Ulva lactuca*	0.1 M HCl	3	32.10	Lupea et al. (2012a)
	Oedogonium sp.	0.5 M HCl	5	27.70	Gupta and Rastogi (2008)
Cu(II)	*Halimeda gracilis*	0.2 M HCl	2	18.30	Jayakumar et al. (2015)
Cr(VI)	*Halimeda gracilis*	0.2 M HCl	10	18.40	Jayakumar et al. (2014)
Cu(II)	*Ulva lactuca*	0.1 M H_2SO_4	3	43.40	Lau et al. (2003)
Ni(II)	*Ulva lactuca*	0.1 M H_2SO_4	3	32.80	
Zn(II)	*Ulva lactuca*	0.1 M H_2SO_4	3	46.60	
Cu(II)	*Gracilaria caudata*	0.5 M $CaCl_2$	2	29.00	Cechinel et al. (2018)
Ni(II)	*Gracilaria caudata*	0.5 M $CaCl_2$	2	11.00	
Zn(II)	*Gracilaria caudata*	0.5 M $CaCl_2$	2	36.00	

Unfortunately, these two major disadvantages (incomplete desorption of toxic heavy metal ions and gradual degradation of the marine algae biomass after each biosorption/desorption cycles) have an important contribution to the limitation of practical applicability of marine algae biosorbents in the removal processes of toxic heavy metal ions from aqueous media on a large scale. Therefore, finding new ways for the valorization of the exhausted marine algae biomasses loaded with toxic heavy metal ions is still an open issue for research.

4.6 Conclusions and Final Remarks

However, the use of marine algae biomass as biosorbents for the removal of toxic heavy metal ions has several important advantages, such as the following:

- Are cheap and available in many regions of the world.
- Their cultivation does not require agricultural soil, so they do not compete with agricultural crops.
- Requires only a few easy and simple stages for preparation.
- Have in their structure various functional groups that easily bind toxic heavy metal ions from aqueous media.

For these low-cost materials have found only few industrial applications at this time.

This is due to the fact that the use of marine algae biomass as biosorbent in the removal processes of toxic heavy metal ions has two important drawbacks, namely, the biosorptive performances of marine algae biomass are lower than the the ion-exchange resins, and the marine algae biomasses have low mechanical resistance and short duration of use, which are responsible for the limited applicability of these versatile materials in the treatment of industrial wastewater.

Under these conditions, the further studies related to the marine algae biosorbents should be directed to the finding of:

(i) Adequate treatments of marine algae biomass that allow for increased of their biosorption capacity and thus to improve their biosorptive performances.
(ii) Adequate immobilization procedures of marine algae biomasses on various supports (often polymeric), which will increase their mechanical strength and life of utilization.

However, the use of marine algae biomass as biosorbent in the advanced treatment of wastewater containing heavy metal ions could be a helpful solution for the efficient treatment of industrial effluents.

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