Sustainable Utilization of Marine Algae Biomass for Environmental Bioremediation

Laura Bulgariu and Dumitru Bulgariu

Abstract The rapid development of anthropogenic activities has a negative impact on the environment, due to the accumulation of harmful heavy metal ions pollutants. Biosorption on low-cost materials has been intensively studied in the last years, because they offer an efficient and cost-effective alternative to the conventional methods used for the environment decontamination. Thus, numerous utilizations of marine algae biomass have been developed for the efficient removal of heavy metal ions from aqueous environments. Unfortunately, such practical applications are not economic efficient. More advantages seem to be the utilization of marine algae biomass as feedstock for energy production. But, even if the obtaining of energy from marine algae is considered a 'clean technology', the valorization of algae waste resulted both after oil extraction and low temperature combustion is still important issue for which further solutions are sought. In this context, the utilization of such marine algae wastes as biosorbent for the removal of heavy metal ions from aqueous media; besides, that will ensure that the utilization of such materials in agreement with the principles of sustainable development will be also helpful in the environment bioremediation processes. In this chapter are comparatively presented the biosorptive performances of marine algae biomass and of wastes resulted from energy production for the removal of various heavy metals ions from aqueous media.

Keywords Marine algae · Metal ions · Biosorption · Energy feedstock
Environmental remediation

L. Bulgariu (✉)
Faculty of Chemical Engineering and Environmental Protection,
Technical University Gheorghe Asachi of Iasi, Iasi, Romania
e-mail: lbulg@ch.tuiasi.ro

D. Bulgariu
Faculty of Geography and Geology, "Al. I. Cuza" University of Iasi, Iasi, Romania

D. Bulgariu
Collective of Geography, Romanian Academy, Filial of Iasi, Iasi, Romania

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1 Introduction

The fuels production and environment protection are two major problems, which are nowadays particularly important for the sustainable development of all societies. The necessity to replace petroleum-derived fuels with renewable biofuels has become one of the most important tools which can be used for environment protection, mainly because the petroleum-derived fuels are well known to have a limited availability and also an important contribution to global warming (Azmir et al. 2013). Although until now, the biofuels production cannot overcome all market requirements, the finding of new and renewable feedstock sources for the biofuels productions has gained increasing attention. From this perspective, the marine algae seem to be one of the potential alternatives that can be successfully used in the production of sustainable energy. The most important advantages of utilization marine algae as feedstock for energy production are

- marine algae are fast-growing plants, available in high quantities in many regions;
- their growth do not require fertile land and freshwater (Demirbas and Karslioglu 2007);
- can convert solar energy into chemical energy with higher efficiency (6–8%) than terrestrial biomass (1.8–2.2%) (Jung et al. 2013);
- marine algae have a lower risk for the competition for food and energy than other crops, because only in few countries from East Asia the marine macroalgae are used as food, fertilizer, and animal feed (Bixler and Porse 2011; Borghini et al. 2014).

Therefore, many experimental studies performed until now have shown that due to their high contents of various carbohydrates, marine algae processing requires less energy that these provides.

There are two ways in which the marine algae biomass can be used for the obtaining of energy, namely: (i) extraction of oil from marine algae biomass and then its transformation in biofuels, and (ii) combustion of algae biomass through a gasification process at relative low temperatures, the resulting gases can be then used to obtain electricity. Both procedures have numerous advantages which have determined the intensification of researches in this field (Demirbas 2009; Patel et al. 2016; Ripoll et al. 2016).

Although the obtaining of energy from marine algae is included in the category of ‘clean technologies’, several environmental drawbacks must still be solved. The most important is the valorization of algae waste resulted both after oil extraction and low temperature combustion, which are usually discharged as waste, or incinerated. A promising alternative for such algae waste could be their use as biosorbent for the removal of heavy metals, and such utilization will be helpful for environmental protection. Besides finding of a use for such waste, the removal of heavy metals using such low-cost materials have important benefits for environment, and these have been recently demonstrated by Life Cycle Analysis studies (Dominguez-Ramos et al. 2014; Maul et al. 2014).

Various heavy metals ions are used in numerous industrial activities, such as: textile, chemical, pigments, storage batteries, plastics, mining, electroplating, smelting, metallurgical processes, etc. (Lyer et al. 2005; Han et al. 2006), due to their technological importance, and are included in the category of persistent environmental pollutants, because cannot be destroyed or degraded (Mehta and Gaur 2005; Park et al. 2010). In addition, due to their mobility, persistency, and accumulation tendency, their presence in natural water ecosystems has serious ecological and human health consequences, when the tolerance levels are exceeded (Aklil et al. 2004; Aydin et al. 2008). Therefore, to prevent the deterioration of environment quality, legislation governing the levels of heavy metals, discharged from industrial waste stream is becoming progressively stricter (Directive 2000/60/EC).

Under these conditions, it has become imperative to maintain or even to improve the quality of environment, the removal the heavy metals from industrial effluents, and this was imposed as a condition of sustainable development. In addition, the recovery of heavy metals from industrial effluents has increasing attention, as society realizes the necessity for recycling and conservation of essential metals (Doble and Kumar 2005; Dhankhar and Hooda 2011).

Various methods have been used for the removal and recovery of heavy metal ions from aqueous effluents. Among these, flocculation, coagulation, chemical precipitation, electrochemical techniques, ion exchange, membrane-related processes, etc. (Dabrowski et al. 2004; Wang and Chen 2009; Llanos et al. 2010) are the most widely used, and now it has been proved that all have numerous disadvantages. Low selectivity and efficiency performances are special when used for small concentrations of heavy metal ions, the necessity of using expensive chemicals in some methods and the generation of high amount of toxic sludge or high energy consumption are the main disadvantages of these methods (Hamdy 2000; Wang and Chen 2009). Therefore it is necessary to find new alternative methods for the removal of heavy metal ions from aqueous environments that minimize these disadvantages, and this is still an actual scientific issue, with great applicative importance.

Biosorption of heavy metal ions, using cheaper and non-living natural materials of biologic origin has become a promising alternative technology, which can offer an ecologically safer, cheaper and more efficient modality to remove metal ions from industrial wastewater. In comparison with conventional methods, the biosorption can be considered a rapid, reversible, economical and eco-friendly method, which can be used in numerous situations to reduce the environmental pollution. In addition, if the biosorption process is well designed, its efficiency is very high, resulting in high-quality aqueous effluents after such treatment, which can be reused without problems. However, the cost of the biosorbents is the most important factor in view of the applicability of the biosorption process in wastewater treatment at large scale.

In order to provide the most cheaper biosorbents, for the removal of heavy metal ions from industrial effluents, various kinds of materials of biologic origin (such as agricultural waste and by-products, algae, fungi, bacteria, peat, yeasts, etc.) (Kurniawan et al. 2006; Febrianto et al. 2009; Farooq et al. 2010; Dhankhar and Hooda 2011) have been intensively tested. In the biosorption processes, such materials act as a chemical substrate and the most important advantages of their utilization as biosorbents are: (a) they have a variety of functional groups on their surface, (b) they have a relatively small and uniform distribution of binding sites on the surface, and (c) require only few steps of preparation, because in most cases these materials result from other industrial or/and agricultural activities. All these advantages have permitted the classification of such biosorbents into category of the low-cost materials.

The marine algae fully meets all these advantages, and because they are available in large quantities in many regions and have an excellent retention capacity, their utilization as biosorbents have been successfully tested for the removal of various heavy metal ions (Donmez et al. 1999; Davis et al. 2003; Romera et al. 2007). However, the utilization of marine algae as a feasible alternative for the energy production (Demirbas and Demirbas 2011; Singh et al. 2011), which is advantageous from economical point of view, has determined the increasing quantities of algae biomass to be used for this purpose. Under these conditions the testing of algae wastes that resulted from energy production for the removal of heavy metal ions could be an alternative utilization which offers the possibility to valorize such materials, which are generally discharged or incinerated, having a serious negative impact on environment.

In this chapter are comparatively presented the biosorptive performances of marine algae biomass and of wastes resulted from algae energy production for the removal of various heavy metals ions from aqueous media. In this way, it is ensured a sustainable utilization of marine algae biomass in environmental remediation, in agreement with the principles of sustainable development. The most important characteristics of each kind of material are highlighted in order to anticipate the potential use of these as biosorbents. Also the biosorptive characteristics of marine algae biomass and of its wastes from energy production as a function of experimental procedure and experimental conditions, along with new updates on biosorption process modelling and some recent advanced in mechanism elucidation are outlined. The results presented in this chapter indicates that the algae wastes from energy production have potential to become effective and economical biosorbents for the removal of heavy metals from industrial waste effluents.

2 Bioremediation of Heavy Metal Ions Using Marine Algae Biomass

Biosorption is one of the most innovative and feasible methods to remove heavy metal ions from industrial wastewaters, which use predominantly non-living algae. Although in the literature are few studies that use living algae for the removal of heavy metal ions from aqueous media (Tsezos and Volesky 1981; Lamaia et al. 2005; Chekroun and Baghour 2013), the important drawbacks of this procedure (such as: low and limited biosorption capacity, poison of algae by heavy metal ions, large variations of biosorptive performances as a function of the growth phase of algae, etc.) have determined the shift of interest to biosorption (Lesmana et al. 2009). In case of biosorption are used non-living algae, which are easier and cheaper to obtained, making the biosorption an economical and effective method to remove the heavy metals from wastewater, and consequently determine the potential remediation capacity using algae biomass.

The biosorption capacity of marine algae biomass depends on several important factors, such as: nature and number of functional groups from algae biomass surface, nature of metal ions from aqueous media, and last but not least by the experimental conditions selected for the biosorption process. Understanding how these factors influence the development of biosorption process will permit the design of high efficient treatment system of industrial wastewaters, and from this reason their discussion must be done.

2.1 Marine Algae Biosorbents

In general, marine algae biomass used as biosorbents for the removal of heavy metals ions are obtained by following few elementary steps, as

(i) collection of marine algae from their natural environment (seas waters);
(ii) washing several times with distilled water to remove the impurities;
(iii) drying in air at temperatures lower than 70 °C (to not damage the algae leaves);
(iv) crushing and sieving until to a given granulation (usually lower than 1 mm).

The obtained biomass is recommended to be stored in desiccators (to keep a constant humidity) and is added to the aqueous media which contains heavy metal ions. Because, the marine algae biomasses are easily obtained and require only few numbers of operations, they can be included in the category of low-cost biosorbents.

Heavy metal ions biosorption onto marine algae biomass has been attributed to the presence of some constituents, such as polysaccharides, proteins or lipids from the cell walls surface that contains different types of functional groups (hydroxyl, carboxyl, amino, sulphate, phosphate, etc.) (Karthikeyan et al. 2007; Gupta and

Rastogi 2008). These constituents are present in the structure of all kinds of marine algae (whether they are brown, red or green algae), and their functional groups play the role of active binding sites for heavy metal ions from aqueous media. The nature of functional groups from marine algae surface has been easy highlighted by FI-IR spectra (Lupea et al. 2012; El-Nerm et al. 2015), and prove the algae biomass will act as a chemical substrate and will bond heavy metal ions from aqueous solutions by characteristic chemical (electrostatic and/or complexation) interactions.

However, the uptake of heavy metal ions from aqueous media significantly depends on the geometrical availability of such superficial functional groups, in consequence the preparation steps will have an important role in the determining of biosorption performances.

2.2 *Influence of Operating Parameters on Heavy Metal Ions Biosorption*

Most of studies from the literature have indicated that biosorption of metal ions onto various low-cost materials of biologic origin occurs with maximum efficiency only in well-defined experimental conditions (Donmez et al. 1999; Febrianto et al. 2009; Robals et al. 2016). These conditions are usually established through batch experiments and aim to study the influence of most important operating parameters on the biosorption process efficiency. Such information are important in the design of adequate wastewater treatment system.

The operating parameters that have a significant influence on the biosorption of heavy metal ion onto marine algae biomass are: initial solution pH, biosorbent dose, contact time, initial metal ions concentration and temperature, and their influence on the heavy metal ions biosorption will permit the finding of optimal values.

(a) ***The influence of initial solution pH***

Initial solution pH is one of the most important operating parameters that affect the biosorption capacity of marine algae biomass for heavy metal ions (Mehta et al. 2002; Rangsayatorn et al. 2002; Han et al. 2006). This is because initial pH solution significantly influences not only the speciation and solubility of metal ions from aqueous solution (free ions or complex species), but also the dissociation degree of functional groups from marine algae biomass surface, considered as biosorption sites (Marques et al. 2000; Esposito et al. 2002).

For a given initial concentration, the heavy metal ions remains as free ions in aqueous solution in relatively large pH intervals (acid to neutral media), and their biosorption occurs without any problems. Unfortunately, high pH values (from weak basic media) may cause the precipitation of metal species. The apparition of precipitation drastically influenced the efficiency of metal ions biosorption and in consequence it should be avoided.

More important is the influence of initial solution pH on the dissociation degree of functional groups from marine algae biomass surface. Therefore, in acid media most of functional groups from are protonated, due to competition between protons and heavy metal ions for the active sites from biosorbent surface (Gardea-Torresdey et al. 1990). This makes the values of biosorption capacity to be low, regardless of the type of metal ions or of marine algae biomass used as biosorbent. The increase in the initial solution pH will determine the increase of dissociation degree of functional groups from marine algae biomass surface. In consequence, the number of electrostatic interactions between metal ions and superficial functional groups will increase and this will be determined by the increase of the biosorption capacities values. In Table 1 are summarized the pK_a values of some functional groups that are relatively abundant in most marine algae biomasses and that have the largest importance in the heavy metal biosorption process.

Therefore, finding the optimal pH for maximum biosorption efficiency is very important step, which must be done experimentally for each studied biosorption system (metal ion and marine algae), because this parameter is correlated with the biomass surface charge, ionization degree and metal ions speciation. In most of cases, the biosorption of heavy metal ions from aqueous media onto marine algae biomass occurs with maximum efficiency in a pH range between 4.0 and 6.0 (Table 2), because in this pH domain the predominant specie of most of heavy metals is free ions (M^{2+}) (Marques et al. 2000) and the dissociation degree of superficial functional groups from algae biomass is high, and will facilitate the electrostatic interactions (Donmez et al. 1999; Sari and Tuzen 2008).

When the heavy metal ions exist in aqueous solution as negative charged species (oxoanions), the weak acid–neutral pH domain is not anymore suitable for the biosorption. The most notorious is the case of Cr(VI), which as is known that in aqueous solution is as CrO_4^- or $Cr_2O_7^{2-}$ species (Kushwaha et al. 2012), and which exhibits a maximum biosorption efficiency onto marine algae biomass in a much lower pH interval (see Table 2). This behaviour is determined by the fact that such negatively charged species could be retained only by the protonated active sites of the biosorbent, and these are obtained in strong acid media (see Table 1), where the concentration of protons is very high (Kayalvizhi et al. 2015; Hackbarth et al. 2016).

Usually, various mineral acid solutions (HCl, HNO_3, H_2SO_4) (Yaqub et al. 2012; Uzunoğlu et al. 2014) or alkali solutions (NaOH, KOH) (Areco et al. 2012)

Table 1 pKa values of most important functional groups from marine algae biomass structure (Dean 1995)

Functional group	Ligand atom	pKa	Functional group	Ligand atom	pKa
Hydroxyl	O	9.5–13	Amine	N	8–11
Carboxyl	O	1.5–5.0	Secondary amine	N	13.0
Thiol	S	8.2–10.8	Imine	N	11.5–12.5
Sulfonate	O	1.5	Imidazol	N	6.0

Table 2 Optimal values of operating parameters for the removal of some heavy metal ions from aqueous media by biosorption on marine algae biomass

Heavy metal ion	Marine algae biomass	pH	Biosorbent dosage (g/L)	Contact time (min)	Temperature (°C)	Reference
Cd(II)	*Fucus ceranoides*	4.5	2.5	25	25	Herrero et al. (2006)
	Fucus serratus	4.5	2.5	25	25	Herrero et al. (2006)
	Bifurcaria bifurcata	4.5	2.5	>60	25	Lee and Chang (2011)
	Saccorhiza polyschides	4.5	2.5	>60	25	Lee and Chang (2011)
	Ascophyllum nodosum	4.5	2.5	>60	25	Lee and Chang (2011)
	Laminaria ochroleuca	4.5	2.5	>60	25	Lee and Chang (2011)
	Pelvetia caniculata	4.5	2.5	>60	25	Lee and Chang (2011)
	Cystoseira baccata	4.5	2.5	17	25	Lodeiro et al. (2006)
	Ceramium virgatum	5.0	0.1	60	20	Sarı and Tuzen (2008b)
	Ulva lactuca	5.0	0.1	60	20	Sarı and Tuzen (2008a)
		5.0	8.0	30	20	Wang et al. (2009)
Co(II)	*Ptredocladia capillacea*	5.0	10.0	<60	25	Ibrahim (2011)
	Galaxaura oblongata	5.0	10.0	<60	25	Ibrahim (2011)
	Ulva lactuca	5.0	8.0	–	23	Lupea et al. (2012b)
Cr(III)	*Spirogyra spp*	5.0	3.0	45	25	Bishnoi et al. (2007)
	Chlorella sorokiniana	4.0	1.0	15–20	25	Akhtar et al. (2008)
Cr(VI)	*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)
	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)
	Ulva lactuca	1.0-1.5	3.0	120	25	El-Sikaily et al. (2007)
Cu(II)	*Fucus serratus*	5.5	0.9	350	25	Ahmady-Asbchin et al. (2008)

(continued)

Table 2 (continued)

Heavy metal ion	Marine algae biomass	pH	Biosorbent dosage (g/L)	Contact time (min)	Temperature (°C)	Reference
	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)
	Ascophyllum nodosum	4.0	1.0	120	Ambient temp.	Romera et al. (2007)
	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)
	Ulva fasciata	5.5	1.0	30	22	Karthikeyan et al. (2007)
	Chaetomorpha linum	5.0	20	120	23	Ajjabi and Chouba (2009)
	Spirogyra spp.	5.0	1.0	30	Ambient temp.	Lee and Chang (2011)
	Cladophora spp.	5.0	1.0	30	Ambient temp.	Lee and Chang (2011)
Pb(II)	*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)
	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)
	Cladophora fascicularis	5.0	2.0	30	25	Deng et al. (2007)
	Spirogyra spp.	5.0	0.5	100	20	Lee and Chang (2011)
	Cladophora spp.	5.0	1.0	30	Ambient temp.	Lee and Chang (2011)
	Ulva lactuca	5.0	0.1	60	20	Sari and Tuzen (2008a)
		5.0	8.0	30	22	Bulgariu et al. (2010)
Ni(II)	*Sargassum glaucescens*	6.0	1.0	120	30	Pahlavanzadeh et al. (2010)
	Padina australis	6.0	1.0	120	30	Kalyani et al. (2004)

(continued)

Table 2 (continued)

Heavy metal ion	Marine algae biomass	pH	Biosorbent dosage (g/L)	Contact time (min)	Temperature (°C)	Reference
	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)
	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)
	Codium vermilara	6.0	0.5	120	Ambient temp.	Romera et al. (2007)
	Cladophora spp.	5.0	5.0	–	23	Zakhama et al. (2011)
	Ulva lactuca	4.5	2.0	60	30	Zakhama et al. (2011)
Zn(II)	*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)
	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)
	Codium vermilara	6.0	0.5	120	Ambient temp.	Romera et al. (2007)
	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. (2006)

are used for adjusting the pH of aqueous solution to the optimal value, before the adding of biosorbent. The choice of the most suitable solution for pH adjustment must be made so as to avoid the apparition of secondary processes (precipitation, complexation, etc.).

(b) *The influence of biosorbent dosage*

The efficiency of heavy metal ions biosorption from aqueous media is dependent on the algae biomass dose. In general, for a given initial heavy metal ion concentration, the increase of biosorbent dose reduces the amount of heavy metals retained per biosorbent unit (Gokhale et al. 2008; Finocchio et al. 2010), determined by the concentration gradient between biosorbent and metal ions from aqueous media. An explanation for this variation could be the fact that at higher dose of biosorbent, the ratio metal ion/algae biomass will be lower, and this will negatively affect the efficiency of biosorption (Mehta and Gaur 2005). High dose of biosorbent determines the apparition of shell effect, which is manifested through the protection of functional groups to be occupied by heavy metal ions, and in consequence the amount of metal ion retained per biosorbent unit will decrease (Farooq et al. 2010). These arguments have made that in the heavy metals biosorption process, lower marine algae biomass dosage has to be recommended.

On the other hand, in the establishment of optimal biosorbent dose must be considered the variation of removal percent also. This parameter depends only on the concentration of heavy metal ions from aqueous media, and it is a measure of biosorption yield. Unlike biosorption capacity (q, mg/g), the removal percent (R, %) increases with the increasing of biosorbent dosage, most probably due to the increase of number of available binding sites (Ucun et al. 2003). In Fig. 1 is illustrated a typical variation of these two parameters (q, mg/g and R, %) as a function of biosorbent dosage, obtained for Cd(II) biosorption onto *Ulva lactuca* sp. marine green algae biomass (Lupea et al. 2012a).

From this reason, the selection of optimal biosorbent dosage must be done after a careful analysis of the experimental values obtained for both parameters (q, mg/g and R, %), to ensure a high biosorptive performance of marine algae biomass (high value of q), but also a high efficiency of biosorption process (high value of R).

In Table 2 are summarized the values of optimal biosorbent dosage found for the biosorption of various heavy metal ions onto different marine algae biomasses.

(c) *The influence of initial heavy metal ions concentration*

The removal of heavy metal ions by biosorption onto marine algae biomass significantly depends on the initial concentration of metal ions from aqueous media. In general, the increase of initial heavy metal ions concentration results on the increase of biosorption capacity of marine algae biomass. This variation is determined to the fact that the increase of initial metal ions concentration provides a large driving force that will overcome all mass transfer resistances between solid

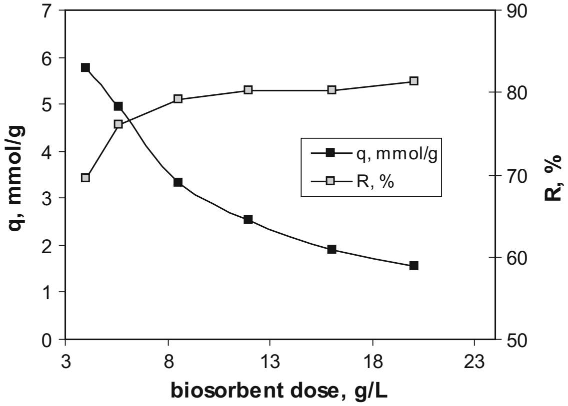


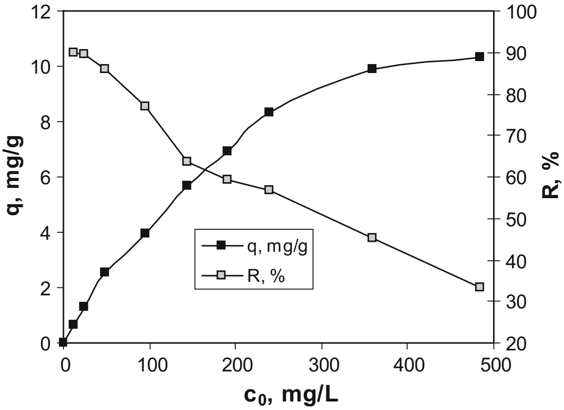
Fig. 1 Influence of biosorbent dosage ob Cd(II) ions biosorption onto *Ulva lactuca* sp. marine green algae biomass

(marine algae biomass) and liquid (aqueous effluents), and in consequence the biosorption of heavy metal ions is higher (Singh et al. 2010). This phenomenon could be used to increase biosorption capacity. For example, Badescu and colab. (Badescu et al. 2015) have reported that the increase of initial Cu(II) concentration from 15 to 210 mg/L determined the increasing of biosorption capacity over 18 times, from 1.12 to 20.28 mg Cu(II)/g dry biomass of *Ulva lactuca* sp. marine green algae. However, it should be noted that this variation is not a linear one. Usually, at very high initial heavy metal ions concentration, the biosorption capacity tends to reach a plateau, which indicates the saturation of biosorbent. For exemplification, in Fig. 2 is illustrated the variation of biosorption capacity of *Ulva lactuca* sp. marine green algae biomass as a function of initial Co(II) concentration (Lupea et al. 2012b).

Such variation of biosorption capacity of marine algae biomasses as a function of initial heavy metal ions concentration indicates that in the biosorption process are mainly involved the functional groups from marine algae biomass surface, and that the interactions between these and the metal ions are most probable electrostatic (ion-exchange type). In a schematic representation, it can be assumed that the heavy metal ions from aqueous media will reach close to the function groups of marine algae biosorbents, where they will interact first with the active sites with largest spatial availability. After these active sites are occupied, they will create a steric blockage that limiting the interactions between metal ions and the functional groups from inside of biosorbent (Bulgariu and Bulgariu 2015).

On the other hand, at low initial concentration of heavy metal ions removal takes place more efficiently than at higher concentrations. This high efficiency is related to the high values of removal percents, which indicate that the concentration of heavy metal ions in effluents treated through biosorption is low (even lower than the values corresponding to the maximum permissible limits (NTPA 002/2005)). Unfortunately, the initial heavy metal concentration interval, where algae waste biomass can be considered an effective biosorbent in the treatment processes of wastewaters, is relatively narrow (>20 mg/L). The increase of the initial

Fig. 2 Influence of initial metal ions concentration on Co(II) biosorption on *Ulva lactuca* sp. marine green algae biomass



concentration of heavy metals over this concentration range results in the increasing of their concentration in effluent solution, and this makes the treatment of wastewaters to be necessary two or more biosorption steps.

(d) ***The influence of contact time***

Heavy metal ion biosorption, using marine algae biomasses as biosorbent, is highly dependent on contact time, and in consequence this parameter should be also optimized. An unsatisfactory value of contact time drastically limits the practical applicability of the biosorption processes, even if the efficiency in the heavy metals removal is high.

Generally, biosorption processes takes place in two subsequent stages: a very fast stage at the beginning, where the amount of heavy metal ions retained increase rapidly within the first minutes (20–60 min), followed by a much slower gradual biosorption, near to the equilibrium. In most of the biosorption processes using marine algae biomasses as biosorbents, no further significant biosorption is noted after 3 h of contact time (Volesky 1987). Therefore, any value of contact time from the second stage can be selected as optimal for a given biosorption system, because here the variation of heavy metal ions biosorption is small. In Table 2 are presented the values of contact time required for the efficient biosorption of heavy metal ions from aqueous media, using different types of marine algae biomasses. It can be observed that the value of optimal contact time is not higher than 180 min in these biosorption processes.

Such two-steps biosorption processes have been reported in many studies from the literature for the retention of heavy metal ions on various low-cost materials (Ho et al. 1996; Gerente et al. 2007; Febrianto et al. 2009; Montazer-Rahmati et al. 2011). The rapid initial biosorption step is generally the result of the fast transfer of metal ions to the surface on the biosorbent particles, while the subsequent slow biosorption process is a consequence of the slow diffusion on metal ions into the pores of the biosorbent particles (Qin et al. 2006). The very fast biosorption of heavy metal ions on marine algae biomass is important from practical point of view, because this will facilitate the scale-up of the biosorption process to smaller reactor volumes, which will ensure efficiency and economy (Liu et al. 2006).

(e) ***The influence of temperature***

The influence of temperature on biosorption efficiency is different as function of the nature of heavy metal ion from aqueous media and type of marine algae biomass used as biosorbent (Monteiro et al. 2010). This parameter is generally used to characterize the biosorption process from thermodynamic point of view, and its optimal value for a given biosorption system must be established experimentally.

Many studies from the literature indicate that the increase of temperature determined the increase of biosorption capacity of marine algae biomass (Gupta et al. 2010; Monteiro et al. 2010; Johansson et al. 2016). Even if the experimental studies have been performed in a relatively narrow temperature range (up to 50 °C, in order to avoid the degradation of algae biomass (Montazer-Rahmati et al. 2011)), such variation of biosorption capacity with temperature indicates that the biosorption process is endothermic one. The main reasons for the increasing of heavy metal ions biosorption with the increase of temperature can be: (i) an increased number of active sites involved in the biosorption process; (ii) an increased availability of active sites from biosorbent surface to interact with heavy metal ions from aqueous media (Mehta and Gaur 2005); (iii) a decrease of mass transfer resistance in the diffusion layer (Meena et al. 2005), and (iv) an increased stability of complex formed between metal ions and superficial functional groups of algae biomass.

The increase of temperature does not always significantly increase the biosorption capacities of marine algae biomass, indicating that temperature has no significant influence on the metal ions biosorption onto marine algae biomass (Martins et al. 2004; Lodeiro et al. 2006). Thus, in the study performed by Lupea et al. (2012a), it has shown that the increase of temperature with 30 °C determine an insignificant variation of biosorption capacity (0.06 mmol/g) of *Ulva lacutca* sp. marine green algae biomass for Cd(II) ions.

In other studies, it was shown that the biosorption of the same Cd(II) ions increase with the increasing of temperature when *Sargassum* sp. or *Ceramium virgatum* are used as biosorbents, because of the exothermic nature of removal process (Cruz et al. 2004; Sari and Tuzen 2008).

In Table 2 is summarized the optimal values of temperature required for the efficient biosorption of heavy metal ions from aqueous media, using different types of marine algae biosorbents. However, analyzing the increase of biosorption efficiency and the costs of temperature increasing, it is recommended that the removal of heavy metal ion from aqueous solutions by biosorption on marine algae biomass is to be performed at ambient temperature, especially by economical considerations (Wang 2002).

Each of these parameters must be analyzed in the experimental studies of heavy metal ions removal by biosorption onto marine algae biomasses, and the obtained results will allow the finding of the optimal conditions that will ensure maximum efficiency of the biosorption process.

2.3 Modelling of Biosorption Process of Heavy Metals on Marine Algae Biomass

In order to understand the biosorption mechanism and to characterize the heavy metals biosorption process onto marine algae biomass, it is necessary to analyze the experimental data both from equilibrium and kinetics point of view. The information obtained from biosorption modelling are very useful for the design of treatment systems of wastewater with large-scale applications.

Therefore, in order to make the biosorption process useful for practical applications it is necessary his mathematical description, and this can be done through modelling. The modelling of biosorption processes implies both the modelling of biosorption isotherms (which represent the equilibrium distribution of the studied heavy metal ions between the phases of the solid biosorbent and aqueous solution) and kinetic modelling (necessary to identify the biosorption mechanism). Practically, the modelling of biosorption process means analyze of the experimental data using various isotherms and kinetics models, and the calculation of characteristic parameters. The selection of the best-fit model is done based on the values of correlation coefficients (R^2), obtained from linear or nonlinear regression.

In case of marine algae biosorbents, the isotherms are usually described with Langmuir and Freundlich models (due to the shape of biosorption isotherms), while the kinetics of biosorption is more frequently analyzed with pseudo-first-order- or pseudo-second-order kinetics models (Chojnacka 2010). The mathematical equations of these models are presented in Table 3.

Although in the literature are presented numerous other models that can be used for modelling, the large applicability of these is determined by their usefulness in the description of heavy metal ions biosorption using marine algae biomass. Thus, the Langmuir model considers that biosorption occurs on homogeneous surface until a complete monolayer coverage is formed at the surface of biosorbent, while the Freundlich model assumes that biosorption takes place on heterogeneous surface and it is not restricted to the formation of a monolayer (Chong and Volesky

Table 3 Mathematical equation of isotherm and kinetics models (Ho 2006; Gerente et al. 2007; Wang and Chen 2009; Febrianto et al. 2009; Montazer-Rahmati et al. 2011)

Model	Mathematical equation	Notations
Isotherm models		
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e$	q_e is the equilibrium metal biosorption capacity; c_e is the equilibrium metal ions concentration in solution; K_F is a biosorption equilibrium constant, representative of the biosorption capacity; n is a constant related with the biosorption intensity
Langmuir	$q_e = q_{\max} \cdot \frac{K_L \cdot c_e}{1 + K_L \cdot c_e}$	q_{max} is the maximum adsorption capacity upon complete saturation of biosorbent surface; K_L is Langmuir constant, related to the biosorption/desorption energy.
Kinetics models		
Pseudo-first model	$\ln(q_e - q_t) = \ln q_e - k_1 \cdot t$	q_e, q_t are the amounts of heavy metals retained on weight unit of biosorbent at equilibrium and at time t, (mg/g); k_1 is the rate constant of pseudo-first order kinetics equation, (min^{-1})
Pseudo-second model	$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e}$	q_e, q_t are the amounts of heavy metals retained on weight unit of biosorbent at equilibrium and at time t, (mg/g); k_2 is the rate constant of pseudo-second order kinetics equation, (g/mg · min)

1995; Rangabhashiyam et al. 2014). Even if the basic assumptions of these models were not fulfilled due to the heterogeneity of the biosorbent surface, they were quite successful in predicting the practical biosorption capacity and optimization of the biosorption system design.

The shape of experimental biosorption isotherms obtained for most removal processes of various heavy metal ions using different types of marine algae biomass is a first indication that these biosorbents have a finite number of available biosorption sites, and in consequence the Langmuir model was found the be best best-fit isotherm model, regardless of experimental conditions. The very well concordance between experimental results and Langmuir model show that the marine algae biosorbents have a surface quite homogeneous and that the biosorption of heavy metal ions from aqueous solution occurs until the formation of monolayer coverage on the outer surface of biomass (Rangabhashiyam et al. 2014). So, it is possible to calculate the maximum biosorption capacity (q_{max}, mg/g) of such biosorbents for a given metal ion in defined experimental conditions, and this could be a measure of biosorptive performances of marine algae biomasses in heavy metals removal processes. In Table 4 are summarized the values of Langmuir model parameters obtained in case of heavy metal ions biosorption on various marine algae biomasses.

Also, the values of Langmuir constant (K_L, L/g) (Table 4), which are related to the biosorption energy (Rangabhashiyam et al. 2014), shows that in most of cases between superficial functional groups of marine algae biomasses and heavy metal ions from aqueous solution occurs strong interaction, most probably of ion-exchange type.

The analysis of experimental date with Langmuir isotherm model indicates that during of biosorption process, the heavy metal ions will interact with the functional groups from out surface of marine algae biomass, predominantly by chemical forces, until entire surface of biosorbent particle will be covered with metal ions. After the coverage of biosorbent particle is complete, the biosorption process does not take place anymore, and the functional groups that could still interact with the metal ions becomes geometrical unavailable.

In comparison with Langmuir model, Freundlich model has a more limited applicability in the mathematical description of heavy metal ions biosorption onto marine algae biomass. This is because the Freundlich isotherm model can be used for the modelling of biosorption processes that occurs on heterogeneous surface or surface supporting sites of different affinity (Farooq et al. 2010), characteristics which are not specific to the marine algae biosorbents. However, in some cases the biosorption of heavy metal ions on marine algae biosorbents are better described by Freundlich isotherm model and several examples are presented in Table 5.

This does not necessarily mean that some marine algae biomasses have a more heterogeneous surface in comparison with other. Most probably in such cases, on the algae biomass surface are present several types of binding sites which have different affinity for heavy metal ions from aqueous solution. Therefore during of biosorption, the metal ions will interact first with the binding sites which have the

Table 4 Langmuir parameters for the removal of some heavy metal ions on marine algae biomass

Heavy metal ion	Marine algae biomass	R^2	q_{max} (mg/g)	K_L (L/mg)	Reference
Cd(II)	*Laminaria* sp.	0.972	104.53	0.01	Delle (2001)
	Oedogonium sp	0.995	88.20	0.02	Gupta and Rastogi (2008)
	Lobophora variegata	0.982	167.91	0.15	Jha et al. (2009)
	Pelvetia caniculata	0.992	75.00	0.07	Lodeiro et al. (2005)
	Cystoseira baccata	0.980	77.56	0.09	Lodeiro et al. (2006)
	Gelidium	0.998	18.0	0.19	Vilar et al. (2006)
	Ulva lactuca	0.988	41.66	0.003	Lupea et al. (2012a)
Cu(II)	*Cladophora* sp.	0.961	47.02	0.14	Deng et al. (2007)
	Fucus serratus	0.993	101.73	0.26	Ahmady-Asbchin et al. (2008)
	Undaria pinnatifida	0.965	78.88	0.06	Chen et al. (2008)
	Ulva fasciata sp.	0.999	26.88	0.25	Kumar et al. (2006)
	Spirogyra sp.	0.995	38.61	0.04	Lee and Chang (2011)
	Laminaria sp.	0.990	61.59	0.02	Liu et al. (2009)
Ni(II)	*Undaria pinnatifida*	0.984	28.89	0.10	Chen et al. (2008)
	Oedogonium sp.	0.985	40.98	0.03	Gupta et al. (2010)
	Laminaria sp.	0.954	66.33	0.02	Liu et al. (2009)
	Cystoseria indica	0.999	47.62	0.03	Pahlavanzadeh et al. (2010)
	Nizmuddinia zanardini	0.999	50.00	0.02	
	Sargassum glaucescens	0.998	52.63	0.02	
Pb(II)	*Cladophora* sp.	0.998	200.42	0.04	Deng et al. (2007)
	Oedogonium sp.	0.998	144.92	0.02	Gupta and Rastogi (2008)
	Nostoc sp	0.990	93.46	0.02	Gupta and Rastogi (2008)
	Lobophora sp.	0.974	580.16	0.11	Jha et al. (2009)
	Cystoseira baccata	0.980	182.33	0.37	Lodeiro et al. (2006)
Zn(II)	*Ulva fasciata* sp.	0.998	13.50	0.09	Kumar et al. (2007)
	Laminaria sp.	0.983	54.26	0.01	Liu et al. (2009)

higher affinity, after that the binding strength decreases with the increase degree of occupation (Febrianto et al. 2009).

But in most of cases, the Freundlich isotherm model is used to estimate the biosorption intensity of heavy metal ions towards a given biosorbent, through n constant (see Table 3). A favourable biosorption process tends to have Freundlich constant n, between 1 and 10 (Delle 2001). Larger value of n (smaller value for 1/n)

Table 5 Freundlich parameters for the removal of some heavy metal ions on marine algae biomass

Heavy metal ion	Marine algae biomass	R^2	n	K_F (mmol g^{-1}) (L $mmol^{-1})^{1/n}$	Reference
Cd(II)	*Laminaria* sp.	0.847	4.98	64.07	Liu et al. (2009)
	Oedogonium sp	0.934	1.63	4.89	Gupta and Rastogi (2008)
	Lobophora variegata	0.906	1.27	17.02	Jha et al. (2009)
	Pelvetia caniculata	0.941	2.80	13.03	Lodeiro et al. (2005)
	Cystoseira baccata	0.970	3.10	75.31	Lodeiro et al. (2006)
	Ulva lactuca	0.910	1.43	0.56	Lupea et al. (2012a)
Cu(II)	*Cladophora* sp.	0.998	2.45	84.38	Deng et al. (2007)
	Fucus serratus	0.978	2.83	161.54	Ahmady-Asbchin et al. (2008)
	Undaria pinnatifida	0.947	1.52	6.65	Chen et al. (2008)
	Ulva fasciata sp.	0.960	0.45	2.22	Kumar et al. (2006)
	Spirogyra sp.	0.958	4.15	9.67	Lee and Chang (2011)
Ni(II)	*Undaria pinnatifida*	0.941	2.52	7.17	Chen et al. (2008)
	Laminaria sp.	0.845	3.78	36.39	Liu et al. (2009)
	Cystoseria indica	0.957	1.77	2.75	Pahlavanzadeh et al. (2010)
	Nizmuddinia zanardini	0.973	1.66	2.09	
	Sargassum glaucescens	0.974	1.63	2.04	
	Padina australis	0.969	1.72	1.08	
Pb(II)	*Cladophora* sp.	0.997	3.62	163.47	Deng et al. (2007)
	Oedogonium sp.	0.925	1.75	8.07	Gupta and Rastogi (2008)
	Nostoc sp	0.949	2.28	8.34	Gupta and Rastogi (2008)
	Lobophora sp.	0.928	1.03	93.24	Jha et al. (2009)
	Cystoseira baccata	0.840	6.00	153.33	Lodeiro et al. (2006)
Zn(II)	*Ulva fasciata* sp.	0.983	0.44	1.42	Kumar et al. (2007)
	Laminaria sp.	0.921	2.92	23.53	Liu et al. (2009)

indicates strong interactions between marine algae biomass and heavy metal ions (see Table 5), while a value of n equal to 1, suggests linear biosorption process, leading to identical biosorption energy for all sites.

Beside the equilibrium modelling, which is very important to characterize the efficiency of biosorption processes, the kinetic modelling it is also necessary to describe the biosorption mechanism. In order to study the biosorption mechanism and its potential rate-controlling step (which can include chemical interactions or mass transport), various kinetic models have been used for the analysis of experimental data. In addition, information on the kinetics of metal ions biosorption on a given biosorbent is necessary in order to obtain optimum operating conditions for industrial-scale metal removal processes (Chojnacka 2010).

It is well known that biosorption is a relatively quick process, in which the equilibrium stage is in most of cases reached within few minutes. The high rate of biosorption makes the selection of proper kinetic model in some cases to be difficult. However, the biosorption processes of heavy metal ions on marine algae biomasses are usually described using pseudo-first-order- and pseudo-second-order kinetics models. The main difference between these two models is that the pseudo-first-order kinetic model assumes that the binding of metal ions from aqueous solution on biosorbent surface is done on only one biosorption site (Eq. (1)):

$$\mathrm{R-O^-_{(solid)}+M^{2+}_{(aq)}\rightarrow R-O^-M^{2+}_{(solid)}} \tag{1}$$

while in case of pseudo-second-order kinetic model, the metal ions are bonded on two binding sites from the biosorbent surface (Eq. (2))

$$\mathrm{2\,R-O^-_{(solid)}+M^{2+}_{(aq)}\rightarrow (2\,R-O^-)M^{2+}_{(solid)}} \tag{2}$$

where: $\mathrm{R{-}O^-}$ is the biosorbent skeleton.

The mathematical equations of these are also presented in Table 3. Based of these linear equations, the fitting of experimental data will allow the determination of biosorption limiting step order and rate constant, which are the characteristic parameters in kinetics modelling. The selection of most suitable kinetic models is done also using the values of correlation coefficients (R^2), obtained from linear or nonlinear regression.

In Table 6 are summarized the values of kinetic parameters of the pseudo-first- and pseudo-second-order kinetic models obtained for the biosorption of some heavy metal ions on various types of marine algae biomasses.

The order of biosorption limiting step is related to the mechanism of biosorption, and in most of biosorption processes that use marine algae biomass the removal of heavy metal ions from aqueous solutions are very well described by the pseudo-second-order kinetic model. According to this model, in the biosorption process the rate limiting step is the chemical interaction (most frequently ion exchange or surface precipitation) between superficial functional groups of biosorbent and heavy metal ions from aqueous solution, which involve valent forces by sharing or exchange of electrons (Ho et al. 1996; Chojnacka 2010). Also, the high values of rate constants (k_2, g/mg · min) obtained in mentioned biosorption

Table 6 Kinetics parameters for the pseudo-second order model obtained in case of some heavy metal ions biosorption on marine algae biomass

Heavy metal ion	Biosorbent	Kinetic parameters			References
		R^2	q_e (mg/g)	k_2 (g/mg · min)	
Cd(II)	*Laminaria hyperborea*	0.997	31.3	0.024	Freitas et al. (2008)
	Sargassum muticum	0.997	38.4	0.004	Freitas et al. (2008)
	Lobophora variegata	0.995	94.2	0.006	Jha et al. (2009)
	Cystoseira baccata	0.999	56.2	0.007	Lodeiro et al. (2006)
	Fucus vesiculosus	0.999	52.8	0.051	Mata et al. (2008)
	Ceramium virgatum	0.999	116.9	0.003	Sarı and Tuzen (2008b)
Cu(II)	*Ulva fasciata*	0.999	9.7	0.013	Karthikeyan et al. (2007)
	Sargassum sp.	0.999	9.6	0.010	
	Fucus vesiculosus	0.999	41.9	0.002	Mata et al. (2008)
Pb(II)	*Laminaria hyperborea*	0.996	50.3	0.020	Freitas et al. (2008)
	Sargassum muticum	0.997	38.2	0.017	Freitas et al. (2008)
	Oedogonium sp.	0.996	117.6	0.064	Gupta and Rastogi (2008)
	Nostoc sp.	0.992	89.3	0.038	Gupta and Rastogi (2008)
	Lobophora variegata	0.967	229.5	0.010	Jha et al. (2009)
	Cystoseira baccata	0.999	142.9	0.001	Lodeiro et al. (2006)
	Fucus vesiculosus	0.999	102.2	0.009	Mata et al. (2008)
Zn(II)	*Laminaria hyperborea*	0.991	19.2	0.075	Freitas et al. (2008)
	Sargassum muticum	0.995	34.1	0.012	Freitas et al. (2008)
	Ulva fasciata	0.976	3.2	0.168	Kumar et al. (2007)

systems (Table 6) show that the rate of the biosorption process is limited by the availability of heavy metal ions and functional groups from biosorbent surface to interact. When the availability of the superficial functional groups is higher, the rate of adsorption process is also higher, and the equilibrium stage is attained very quickly.

The very well concordance between experimental data and pseudo-second kinetic model is reported in the literature for various types of adsorbent materials of biologic origin (Wang and Chen 2009; Febrianto et al. 2009; Montazer-Rahmati et al. 2011), and the main advantage of this model is its high accuracy in describing the whole kinetic experimental data.

2.4 Overview on Marine Algae Biosorbents

As it was discussed previously, the biosorption processes which used marine algae biomass as biosorbents is a very useful tool in the treatment of aqueous effluents contaminated with metal ions, mainly due to their advantages such as economic and technologic viability, quantitative release of retained metal ions, minimization of secondary waste, easy of operating, high efficiency, low cost of biosorbents preparation, etc. (Romera et al. 2007; Wang and Chen 2009).

Although, such biosorption studies have been performed still from the middle of last century (Tuhy et al. 2014) this skilful method has found no industrial applications at this moment, this method has found no industrial applications at this moment. This is because the utilization of marine algae biomass for the heavy metal ions biosorption has several drawbacks which must be still solved. The most important of these are

(i) ***the biosorption capacity of marine algae biomass for various heavy metal ions, is in most of cases lower that the ion exchange resins***. In order to solve this problem, the researches have been directed to the utilization of various physical and chemical treatments of marine algae biomass that changes the algae surface properties and that provide additional binding sites for the heavy metal ion uptake. Thus, the treatments such as heating/boiling, freezing, crushing, chemical treatments with various reagents (mineral acids, alkali, common inorganic salts, organic compounds), etc., have followed to enhance the metal ions biosorption on marine algae biomass (Ebrahimi et al. 2009, Bulgariu and Bulgariu 2014). Such treatments act to the surface of cell walls membrane and in most of cases provides a greater number of active sites, which determine the increase the biosorption capacity. Unfortunately, the increase of biosorption capacity of marine algae biomass after such treatments is not always a spectacular one, especially considering that the enhancement of biosorption capacity must done without using additional expensive additives, and so the cost of biosorbent preparation remains low (Bulgariu and Bulgariu 2014).

(ii) ***the marine algae biomasses have low mechanical resistance and short life of utilization***. Thus, the easiest technological operations (as pumping or mixing) can destroy the fragile structure of marine algae biomass, which will drastically influence the efficiency of biosorption process. On the other hand, the same mechanically fragile structure of marine algae biomass is also responsible by the short life of utilization of these biosorbents, because their regeneration and reuse is sometimes difficult to achieve. In order to overcome this inconvenient, many studies from the literature have reported the possibility to immobilize marine algae biomasses on various supports. Various natural polymer (such as agar or alginate) or synthetic compounds (such as silica gel or polyacrylamide) have been used as supporting materials for the immobilization of marine algae biomass (Bayramoğlu et al. 2006; Montazer-Rahmati et al. 2011). The natural polymers are often preferred to synthetic polymers due to non-toxicity on biomass, but the use of this procedure makes that some functional groups from algae biomass surface to become unavailable for metal ions from aqueous solution, because they are blocked by interactions with the polymer matrix. Therefore, even if the mechanically resistance of such immobilized marine algae biomass is significantly improved, their efficiency in biosorption processes of heavy metal ions is often lower (Singh et al. 2011).

(iii) ***the utilization of marine algae biomass in the treatment of wastewater may cause secondary pollution of aqueous effluents***. The secondary pollution appears due to the dissolving of some organic compounds from the biomass structure during biosorption and it is responsible for the increasing of oxygen demand (CCO index) of treated effluent, which is also undesirable because affects its quality. A solution for this problem could be the use of marine algae biomass; first to obtain the oil necessary for the production of biofuels, and then as biosorbent to remove the heavy metal ions from aqueous media. In this way, the easily soluble organic compounds from biomass structure are eliminated since the extraction step, and the resulting material will act as a chemical substrate of biological origin, where superficial functional groups are strongly bonded to the biomass skeleton (Bulgariu and Bulgariu 2012, 2013).

The careful analysis of these drawbacks makes necessary the re-evaluation of technological aspects related to biosorption processes which use marine algae biomass as biosorbent for the removal of heavy metal ions, in order to highlight their feasibility for practical applications.

3 Bioremediation of Heavy Metal Ions Using Marine Algae Waste Biomass

In the last years, the necessity to cover the fuel market requirement has made that large quantity of marine algae biomass to be used for production of biofuels (Singh et al. 2011; Halim et al. 2011). In addition, the extraction of oil from marine algae biomass for biofuels production has proved to be more economical efficient than the removal of heavy metals from industrial wastewater. After oil extraction step, the remaining algae biomass is considered a waste and it is usually discharged or incinerated, becoming a serious problem for environmental protection (Sims et al. 2010). Until now, only few studies from literature have shown that this waste biomass can be used as low-cost biosorbent for the removal of heavy metals from aqueous media (Bulgariu and Bulgariu 2013, 2016; Xie et al. 2014), even if for such biosorbents the effect of secondary pollution is drastically minimized.

3.1 Marine Algae Waste Biosorbent

In the most general way, the algae waste biomasses are obtained from algae biomass, after solvent extraction operations, when certain types of components (such as lipids, fatty acids, other compounds) are extracted from algae biomass structure (Bulgariu and Bulgariu 2015). The extraction step is performed with common organic solvents (most frequently used being n-hexane or benzene) in Soxhlet extractors and the analysis of the obtained waste biomass has show that

(i) the content of C, O, S and P slightly decreased, suggesting that only certain components from the biomass composition were removed through solvent extraction.

(ii) the specific surface area significantly increase after extraction step, mainly due to the disruption of walls cells of marine algae. Thus, after oil extraction with n-hexane an increase of BET surface area from 0.56 m^2/g to 1.71 m^2/g in case of *Chlorella vulgaris* algae (Xie et al. 2014), and from 0.63 m^2/g to 1.28 m^2/g in case of *Ulva lactuca* algae (Bulgariu and Bulgariu 2015) is reported in the literature. The scanning electron microscopy images presented in these studies confirm that after extraction step, the surface of marine algae waste biomass becomes more irregular, and probably these irregularities are responsible by the increase of specific surface area of biosorbent.

    Due to the presence of these irregularities the mass transfer resistance inside of pores decrease, which will facilitate the metal ions diffusion, and thus will contributing to the improvement of biosorption process efficiency (Yeh and Chang 2012).

(iii) IR spectra indicate that most functional groups from marine algae biomass structure are not affected by the extraction step, and most of absorption peaks from FT-IR spectra remains unchanged. Thus, in case of *Ulva lactuca* marine green algae after oil extraction with n-hexane, (Fig. 3), only the absorption bands corresponding to the easy extractable compounds (such as lipids, cerides, etc.) disappear or decrease in intensity. All others functional groups (such as: hydroxyl, amine, carbonyl, carboxylic groups, etc.) from polysaccharides and proteins remain in the structure of waste biomass, and these may interact with heavy metals during of biosorption process.

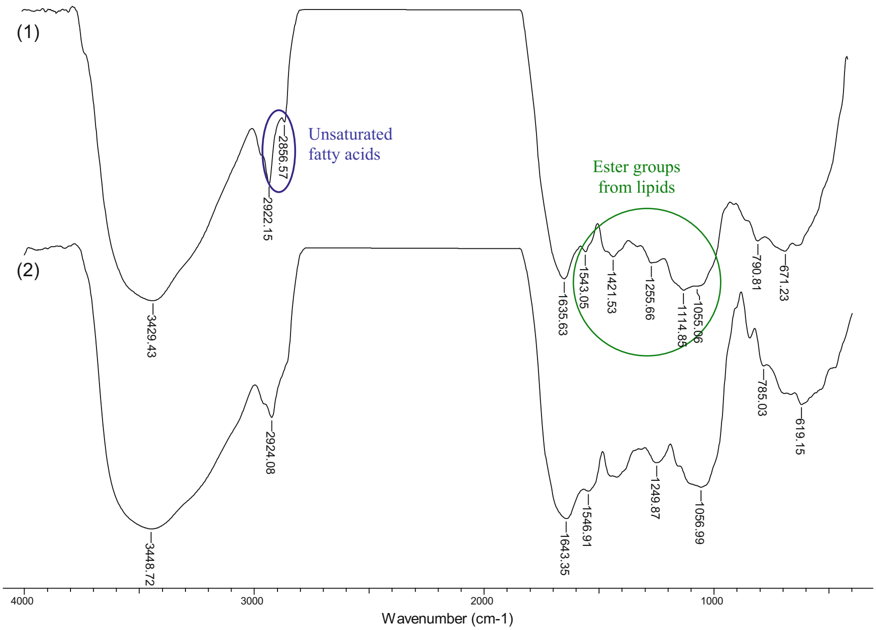


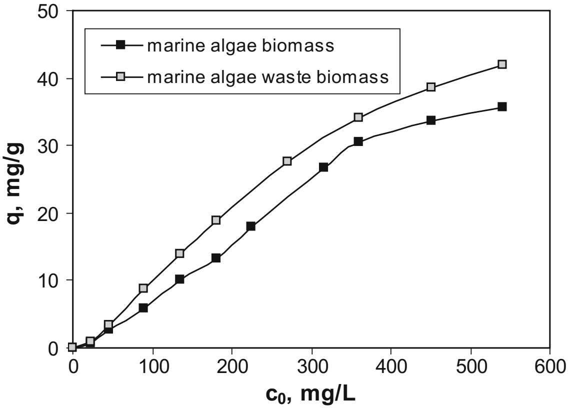
Fig. 3 IR spectra of *Ulva lactuca* sp. marine green algae biomass before (**1**) and after (**2**) extraction of oil with n-hexane

On the basis of these observations it can be said that in case of marine algae biomass, the nature of functional groups responsible for the heavy metal ions uptake is not significantly changed, but their number is improved mainly due to the disruption of walls cells, during of extraction. After extraction, the obtained waste biomass should be washed to remove impurities, dried in air at a given temperature (50–60 °C) for a determined period of time, crushed and sieved to a given particle size (1.0÷1.5 mm), and stored in desiccators for its use as biosorbent.

3.2 Evaluation of Biosorptive Performances of Marine Algae Waste Biosorbents

Since the nature of functional groups is not changed too much, it is expected that the maximum efficiency of biosorption processes that use marine algae waste biomass as biosorbents are to be obtained in the same optimal conditions (initial solution pH, biosorbent dosage and temperature) as in case of marine algae biomass. Only the initial metal ions concentration and contact time may change significantly, because these operating parameters are related to the number of superficial functional groups. Therefore, in order to evaluate the biosorptive performances of marine algae waste biomass, the influence of initial metal ion concentration and

Fig. 4 Influence of initial metal ions concentration on Cd(II) biosorption on *Ulva lactuca* sp. marine green algae biomass, before and after extraction step



equilibrium contact time on the biosorption efficiency must be examined, in comparison with un-extracted marine algae.

In the few studies from literature on this topic (Long et al. 2014; Bulgariu and Bulgariu 2015) it was shown that the marine algae waste biomass has better biosorptive performances than marine algae biomass, and this improvement is more evident at high initial heavy metals concentration. In Fig. 4 is illustrated, for exemplification, the variation of the amount of heavy metals retained on weight unit of biosorbent (q, mg/g) as a function of initial Cd(II) ions concentration, when is used *Ulva lactuca* sp. before (marine algae biomass) and after extraction step (marine algae waste biomass).

These experimental results suggest that in the biosorption mechanism of Cd(II) onto marine algae and marine algae waste biomass are involved, predominantly electrostatic (ion exchange) interactions and the efficiency of biosorption process depends on the availability of functional groups from biosorbent surface. Thus, when the marine algae biomass is subjected to the solvent extraction process, this will break the cell walls of algae, and will spatially activate some functional groups that were inactive before. In consequence, the biosorption capacity of obtained biosorbent will increase. The change of functional groups availability after solvent extraction step have determined a growth of biosorption capacity of *Ulva lactuca* sp. marine algae biomass with 20–30%, for heavy metal ions as Pb(II), Cd(II), Co (II) or Zn(II) from aqueous media (Bulgariu and Bulgariu 2012, 2016), and thus is increased the economical feasibility of this biosorbent.

On the other hand, the equilibrium modelling of obtained isotherms indicate that Langmuir model best describe the experimental results in all cases, indicating the forming of monolayer coverage of the heavy metal ions on the outer surface of the marine algae waste biomass. In Table 7 are summarized the values of maximum biosorption capacity (q_{max}, mg/g) of marine algae biomass and marine algae waste biomass obtained from Langmuir isotherm equation, for the biosorption of some heavy metal ions.

Table 7 Comparative values of maximum biosorption capacity (q_{max}, mg/g) and contact time for the biosorption of some heavy metal ions on marine algae and marine algae waste biomass (Bulgariu and Bulgariu 2012; Lupea et al. 2012a, b)

Metal ion	Marine algae biomass		Marine algae waste biomass	
	q_{max}, (mg/g)	t (min)	q_{max}, (mg/g)	t (min)
Pb(II)	58.13	60	66.30	20
Cd(II)	27.81	60	34.85	40
Co(II)	9.89	60	16.50	20

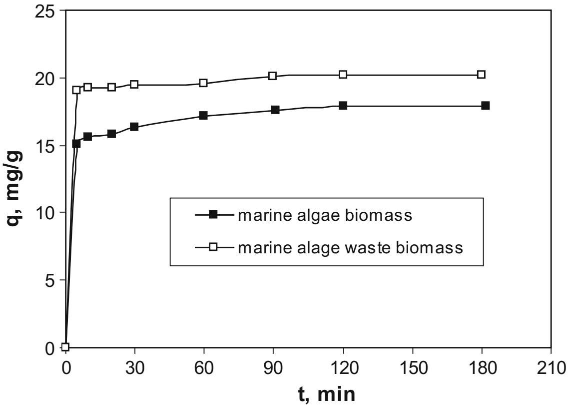
It can be observed that the values of maximum biosorption capacity (q_{max}, mg/g) were slightly higher in the case of marine algae waste biomass, than in case of marine algae biomassThe increase of this parameter clearly shows that the specific surface area of biosorbent has been increased, and in consequence a high number of metal ions are required to form complete monolayer coverage.

On the other hand, by studying the effect of contact time between biosorbent (marine algae biomass and marine algae waste biomass) and heavy metal ions from aqueous solution, it can be observed that the biosorption efficiency increased along contact time, as is expected. For exemplification, in Fig. 5 is illustrated the influence of contact time on the Pb(II) ions biosorption efficiency, when is used *Ulva lactuca* sp. before (marine algae biomass) and after extraction step (marine algae waste biomass) as biosorbents.

Beside an increase of biosorption efficiency along of contact time, which is normal in case of heavy metal ions biosorption processes, these results have shown another important advantage in the using of marine algae waste biomass as biosorbent, namely that the required time for the biosorption process is significantly lower. Several examples are also summarized in Table 7.

The lower values of contact time necessary to reach the equilibrium state in case of marine algae waste biomass is one more argument which sustains the hypothesis of the biosorption process of heavy metal ions that occurs predominantly by

Fig. 5 Influence of contact time on Pb(II) biosorption on *Ulva lactuca* sp. marine green algae biomass, before and after extraction step



electrostatic interactions (between positive charged metal ions and negative charged functional groups), and is influenced by the availability of functional groups to interact. If the availability of superficial functional groups is higher, the rate of biosorption process is also higher. Therefore, when the marine algae biomass is used first in solvent extraction step, the disruption of cell walls makes that the functional groups from resulted biomass to be more available for the interactions with metal ions from aqueous solution. In consequence, the rates of biosorption processes on such biosorbents are higher, even with one order of magnitude, than in case of marine algae biomasses (Bulgariu and Bulgariu 2016).

3.3 Overview on Marine Algae Waste Biosorbents

Although, the utilization of marine algae waste biomass as biosorbent (instead of marine algae biomass) for the biosorptive removal of heavy metal ions from aqueous media significantly reduces the secondary pollution of treated effluents, several technical aspects must be solved before such materials to be used for wastewater treatment, at large scale. The most important are (Bulgariu and Bulgariu 2016)

(i) the removal of the traces of organic solvents from biomass by a simple procedure which does not involve high temperatures (because at high temperatures the biomass structure can be destroyed and the number of functional groups reduced);
(ii) improving of the algae waste performances in biosorption processes (because low biosorption capacities generate large amounts of biomass loaded with heavy metals that is also an environmental problem) (Long et al. 2014);
(iii) prevention of column clogging in continuous systems, which due to the small size of biomass particles (necessary to ensure the high efficiency of oil extraction process), does not allow the proper passage of aqueous solution.

The treatment of marine algae waste biomass with alkaline solutions (ex. 0.1 N NaOH solution) has been proposed in literature (Bulgariu and Bulgariu 2014, 2016) to solve the first two problems. As it is shown in these studies, the alkaline treatment of marine algae waste biomass has two essential roles, namely: (i) reducing the hydrophobicity of the biomass surface, which makes that the traces of organic solvents remained from the extraction step to be eliminated at usual drying temperature (55–60 °C), and usually in a single heat treatment stage, and (ii) improves the dissociation degree of most superficial functional groups, and thus will increase the number of binding sites from the biomass surface (Bulgariu and Bulgariu 2014). These solutions have been chosen so that the cost of obtained biosorbent remains low and without the need of taking supplementary steps for its preparation.

Beside the immobilization of marine algae waste biomass in polymer matrix, which is described in the literature as one of the possibilities that permit the utilization of such biosorbents in continuous treatment systems, our previous studies (Bulgariu and Bulgariu 2013, 2016) have indicated that the mixing of marine algae waste biomass with a cheap and commercially available anion exchanger resin, such as Purolite A-100, could be also an option. The mixing of marine algae waste biomass with Purolite A-100 resin (considered an inert material with respect of most of heavy metal ions) can be done mechanically, and this procedure has been shown to be effective because it ensures the passing of aqueous solution through the column in a wide flow rate range.

However, the marine algae waste biomasses are still characterized by a low mechanical resistance, and the minimization of this drawback remains a challenge for the further researches, in order to design continuous treatment systems of wastewater contaminated with heavy metal ions.

4 Bioremediation of Heavy Metal Ions Using Marine Algae Biochar

Beside the biofuels production, another procedure that can be used for green energy production and that has gained increased credibility in the last years is the biomass gasification (Heidenreich and Foscolo 2015). Generally, the gasification supposes the transformation of biomass in gases, which may be then used to obtain energy in turbines or boilers (Lan et al. 2015). In case of marine algae biomass or marine algae waste biomass utilization in gasification processes has two major advantages:

(i) the volume of biomass waste is considerable reduced (up to 75%), which represents an important benefit for environment;
(ii) the cost of energy production is lower in comparison with classical combustion methods, because these processes generally occurs at relatively low temperatures (until 500 °C) and in low-oxygen atmosphere (Asadullah 2014; Mohan et al. 2014).

The solid material remained after algae biomass gasification, generally called biochar, is mostly controlled deposited or used for the manufacture of building materials (Agarwal et al. 2015). Nevertheless, the preliminary experimental studies performed by us have shown that such biochar has structural and textural characteristics which recommend it as potential biosorbent in decontamination processes of environment.

Unfortunately because the nature of algae biomass used as feedstock for biochar production, and the thermal treatment conditions (particularly temperature, but also the treatment time it is important), strongly affect the biosorptive characteristics of obtained biochar, it is still a need to undertake detailed studies about the possibility to use this material as biosorbent for heavy metal ions removal (Bird et al. 2011; Maddi et al. 2011).

4.1 Marine Algae Biochar Biosorbent

The changes that occur in the structure of marine algae biomass after its transformation in biochar through thermal treatment can be easy highlighted using IR spectra. The IR spectra recorder in case of *Ulva lactuca* sp. marine algae biomass before and after thermal treatment at 450 °C, illustrated in Fig. 6, clearly shows this.

Thus, after thermal treatment the IR spectra of marine algae biochar (spectra b) indicate that the most adsorption bands are less split, probably due to the breaking of physical bonds between functional groups of marine algae biomass. Also after thermal treatment, the most important functional groups from biomass surface are converted in their reduced form (for example: hydroxyl groups (3429 cm^{-1}) and carbonyl or ether groups (1635 cm^{-1})). Another significant difference is the drastically intensity decrease of the peak from 2922 cm^{-1} that correspond to the C–H stretching vibration of aliphatic hydrocarbons radicals. The significant decrease of this peak shows that after thermal treatment most of aliphatic hydrocarbons chains from marine algae biomass structure were removed by thermal treatment (probably as CO_2 and H_2O), and the obtained biochar contains predominantly aromatic scraps.

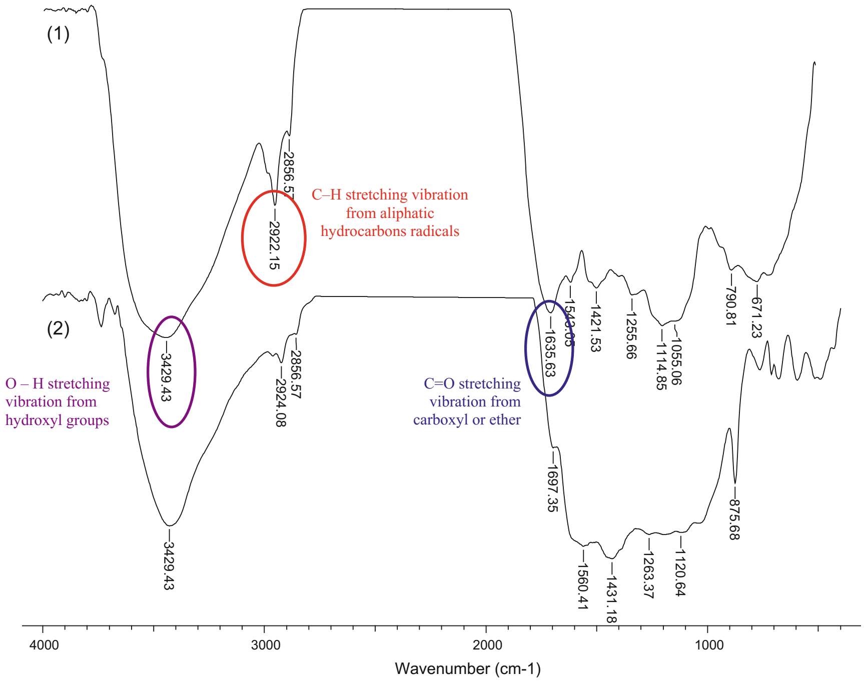


Fig. 6 IR spectra of *Ulva lactuca* sp. marine green algae biomass before (**1**) and after (**2**) thermal treatment

The analysis of IR spectra it allows us to say that

(i) in the structure of marine algae biochar are still sufficient functional groups that can bind heavy metal ions from aqueous media—so such material can be used as biosorbent for the removal of heavy metal ions from aqueous media;
(ii) due to the thermal treatment, the biochar has a high specific surface area, which may also represent an advantage in the heavy metals biosorption processes.

4.2 Evaluation of Biosorptive Performances of Marine Algae Biochar

In order to evaluate the biosorptive performances of marine algae biochar it was considered the influence of initial metal ions concentration and contact time on the biosorption efficiency. The experimental results presented in literature (Johansson et al. 2016; Park et al. 2016) have shown that in comparison with marine algae biomass, the marine algae biochar has higher biosorption capacity, in the same experimental conditions. In Fig. 7 is presented for exemplification the variation of biosorption capacity (q, mg/g) as a function of Pb(II) concentration in case of *Ulva lactuca* sp. marine algae biomass and biochar obtained from this biomass after thermal treatment at 450 °C during of 4 h.

It can be observed that the biosorption efficiency of marine algae biochar increases rapidly as a function of the initial Pb(II) concentration, and there was no evidence that the biosorbent attains the saturation, for entire initial Pb(II) concentration range.

The good biosorptive performances of marine algae biochar, obtained in this case, has probably mainly two causes: (i) the formation of very high number of mesopores and macropores in the structure of biochar, which are responsible by the

Fig. 7 Influence of initial metal ions on Pb(II) biosorption on *Ulva lactuca* sp. marine green algae biomass, before and after thermal treatment

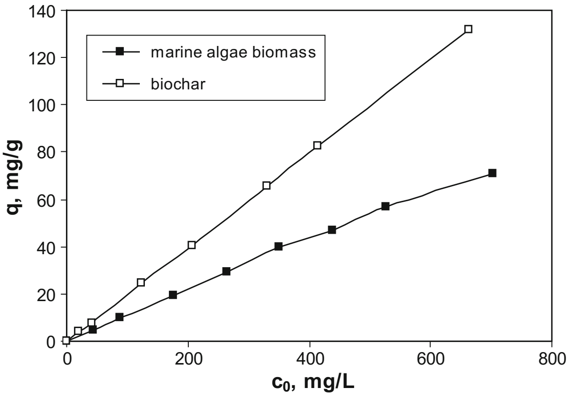
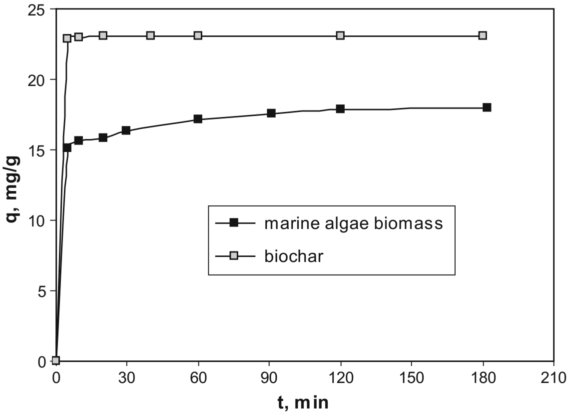


Fig. 8 Influence of contact time on Pb(II) biosorption on *Ulva lactuca* sp. marine green algae biomass, before and after thermal treatment



increase of specific area of this biosorbent, and (ii) the increase in the quantity of exchangeable cations by activation, which has an important contribution to the biosorption process of Pb(II) ions (Bulgariu 2016; Park et al. 2016).

The equilibrium modelling of experimental isotherms obtained by using marine algae biochar shows that and in this case the Langmuir model is the most adequate for the mathematical description of heavy metal ions biosorption, and the values of maximum biosorption capacity (q_{max}, mg/g) necessary for the formation of monolayer coverage are much higher than those obtained in case of utilization of marine algae biomass as biosorbent, in the same experimental conditions Thus, in case of Pb(II) biosorption on marine algae biochar the value of q_{max} was 5.32 times higher than the value obtained for using marine algae biomass as biosorbent (Bulgariu 2016).

Another important advantage of using marine algae biochar for the removal of heavy metal ions from aqueous media is the required time to attain the equilibrium of biosorption process is very short. For example, in case of Pb(II) ions the maximum removal efficiency (>95%) was obtained within 5 min in case of marine algae biochar, in comparison with 60 min, when marine algae biomass is used as biosorbent (Fig. 8).

Similar results have been also reported in literature for the biosorption of various heavy metal ions biosorption on such biochars (Jung et al. 2015; Inyang et al. 2016; Kim et al. 2016). In addition, in all these cases the kinetics data comply with the pseudo-second-order kinetics model, which suggest that the biosorption process has a certain selectivity degree, due to the chemical interaction which is the rate-controlling step.

In addition, the result reported in literature suggests the possibility of using marine algae biochar for the removal of heavy metal ions from accidental polluted waters. Thus, the low value of contact time required to attain biosorption equilibrium state indicate that immediately after adding the marine algae biochar the heavy metal ions are quantitatively retained on biosorbent surface. After the biosorption process is ended, the biochar particles covered with heavy metal ions can be easy removed from waters by filtration, and thus the pollution risk of environment is eliminated.

4.3 Overview on Marine Algae Biochar Biosorbents

The use of marine algae biochar as biosorbent for the removal of heavy metal ions from aqueous media is a relatively new research direction, which has been more intensively developed in the last few years. From this reason, experimental studies must be still carried out in order to obtain a general picture over the biosorptive performances of this kind of biosorbent material in the environmental remediation processes.

Until now, the experimental results are encouraging, and highlight at least two advantages for the utilization of marine algae biochar as biosorbent for the removal of heavy metal ion, namely: (i) this material is a waste resulted from the production of green energy where as feedstock is used marine algae biomass, which is also a low-cost material, and (ii) the biosorption efficiency of the biochar obtained after thermal treatment of marine algae biomass seems to be higher in comparison with initial material.

5 Final Remarks

The removal of heavy metal ions from aqueous media by biosorption using marine algae biomass as biosorbents, has several important advantages over conventional wastewater treatment methods, including: high efficiency of heavy metal removal from dilute solutions; minimization of chemical and/or biological waste; economic viability; ease of use; etc.

Marine algae biomasses are usually considered low-cost materials and their utilization as biosorbents is determined by the large number and variety of functional groups from biomass surface, which is complemented by the relatively small and uniform distribution of binding sites on biosorbent surface.

Although the algae biomass have been proved to be an excellent biosorbent for heavy metals removal, this utilization is not very efficient from economic considerations. More efficient from this point of view it is the utilization of marine algae biomass as feedstock for energy production, and from this reason larger quantities are used for this purpose.

In literature are described at least two ways in which the marine algae biomass can be used for the obtaining of energy, namely: (i) extraction of oil from marine algae biomass and then its transformation in biofuels, and (ii) combustion of algae biomass through a gasification process at relatively low temperatures, the resulting gases can be then used to obtain electricity. Both procedures have numerous advantages what have caused the intensification of researches in this field.

Unfortunately, even if the obtaining of energy from marine algae is considered a ‘clean technology’, the valorisation of algae waste resulted both after oil extraction and low temperature combustion is still important issue for which further solutions are sought. In this context, the utilization of such marine algae wastes as biosorbent for the removal of heavy metal ions from aqueous media besides that will ensure the utilization of such materials in agreement with the principles of sustainable development will be also helpful in the environment bioremediation processes.

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