Bioadsorption of Heavy Metals

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Abstract Pollution caused by heavy metals is one of the most serious environmental problems for society. Industrial activities increase the concentration of heavy metals such as Cu(II), Cd(II), Zn(II), Pb(II) and Ni(II) in aquatic systems and mainly in the fields of mechanics, electrics, electronics, tanning, galvanization, oil industries and mining. Biomagnification of these metals occurs through the toxicity of the trophic for humans. As a remedial measure, it is for scientists to find new biosorbents which are able to ameliorate the possible toxic effects of heavy metals in water bodies. Studies of bioadsorption have identified this as a real alternative to wastewater treatment, especially for the removal of heavy metals. This chapter explores (1) the characterization of new biosorbents via surface acid–base titration, where the type of functional groups can be tentatively computed, (2) kinetics of bioadsorption (pseudo-first and second order), (3) bioadsorption as a function of pH and (4) bioadsorption as a function of metal concentration in solution (Langmuir, Freundlich, Sips, Redlich–Peterson, Tóth, Frumkin and Temkin isotherms), where the maximum adsorption capacity can be determined under different experimental conditions. The majority of bioadsorption studies have been carried out at laboratory scale; however, future studies will be conducted at industrial scale as a way to

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remediate heavy metal pollution in water bodies. Different commercial biosorbents and their characteristics are presented in this chapter.

1 Introduction

Environmental pollution is one of the most pressing issues for our society, and one of the unsolved questions in this respect is how to decrease pollution by heavy metals, especially in water bodies where these metals are released as a result of the increased industrial activity. The presence of heavy metals such as Cu(II), Cd(II), Zn(II), Pb(II) and Ni(II) is directly linked to their use in a number of industrial activities such as mechanics, electrics, electronics, tanning, galvanization, oil industries or mining (Abdel-Ghani and El-Chaghaby 2014), being toxic for humans and ecosystems (Meena et al. 2008). These metals are not biodegradable and have long resident times in aqueous environments. This environmental phenomenon is of particular significance for humans due to the biomagnification of these metals through the trophic web, creating gastrointestinal, neurological and immunological hazards. Therefore, it is vital for the scientific community to continue research into new biosorbents in order to ameliorate the effect of heavy metal pollution in water bodies, aiming at identifying economical and eco-friendly biosorbents.

Since the 1950s, great advances have been made in the study of sorption of heavy metals on different biomaterials, aiming at finding an efficient, effective, economical and eco-friendly biosorbent. During this time, the knowledge about complex biosorption mechanisms and models has been enhanced. In terms of patenting, bioremediation has achieved 237 patents since 1975 (Jara et al. 2016). 137 of these patents and more than 1500 research papers have addressed algae as biosorbents due to their high adsorption capacity (Michalak et al. 2013). However, most of this scientific work has taken place at laboratory scale, making it necessary to transfer it to the industrial scale. Bioadsorption is becoming a potential alternative for wastewater treatment, especially for the removal of heavy metal, even though a lot remains to be learned before application to the industrial scale can be considered, especially due to the low stability and low mechanical resistance of the biomass. Bioadsorption holds many advantages compared to other types of treatment, for instance, high efficiency for low metal concentrations, efficiency for a wide range of pH and temperature conditions, easy recuperation of adsorbed material, as well as easy and cheap production of biomass. Bioadsorption offers the added advantage of working with non-living biomass, reducing the possibility of contamination, toxic effects and metabolic activities.

It is important to distinguish between bioadsorption and bioaccumulation since both are commonly used to remove heavy metals from solutions:

Bioadsorption is a physico-chemical process in which the concentration of sorbate (heavy metals) is adsorbed on the bio-surface. In general, this biological surface is not living biomass. Consequently, it is a metabolically passive mechanism, a rapid and reversible mechanism binding metal ions from aqueous solutions onto functional groups.

Bioaccumulation or bioabsorption refers to a sorbate accumulated into the cells. Therefore, bioaccumulation is a metabolically active process which follows the first step, bioadsorption.

The adsorption of heavy metals on the surface of a biosorbent is a physico-chemical mechanism including different processes such as electrostatic interaction, complexation, ion exchange or proton displacement (Davis et al. 2003; Volesky 1990; Crist et al. 1999). This adsorption process is affected by many physico-chemical conditions, not only those affecting the biosorbent but also those of the sorbate and media such as molecular weight, ionic radius, oxidation state, the concentration of both adsorbent and sorbate, biosorbent properties, pH, temperature, ionic strength, etc.

In order to propose a new biosorbent, it should be precisely characterized in terms of adsorption. This requires consideration of the presence of functional groups on the cell surfaces, adsorption capacities, both as a function of pH and metal concentration in solution, kinetics of adsorption, as well as other factors such as temperature and biomass.

2 Characterization of Biosorbents

2.1 Surface Acid–Base Titration

Surface acid–base titrations provide a measure of sequential binding of protons by the various functional groups on the surface of the algae, and the variation in that portion of the charge caused by H^+ binding (González-Dávila 1995; González-Dávila et al. 1995; Stumm and Morgan 1981). This allows us to quantify the proton and hydroxyl buffer capacities of biosorbents in a wide range of pH and thus determine the proton binding capacity and the concentration of amphoteric surface functional groups on biosorbents.

The excess surface proton concentration can be calculated as (Martinez et al. 2002; Cox et al. 1999; González et al. 2010; González and Pokrovsky 2014):

$$[H^+]_s = \left(\left(C_{aj(suspension)}\right) - \left(C_{aj(reference)}\right)\right) - \left(\left(C_{bj(suspension)}\right) - \left(C_{bj(reference)}\right)\right) \quad (1)$$

where C_{aj} and C_{bj} correspond to the concentration of base and acid for the jth addition of titrant, respectively. As a reference system, the supernatant from the rinsed biosorbent biomass is used and processed exactly in the same way as biosorbent suspension. Note that this definition of excess surface proton concentration does not allow direct conversion to the cell surface charge, as the initial amount of surface protons is not known.

The acid–base titration experiments have been modelled by considering that the proton dissociation mechanisms for a single protonated site correspond with the following:

$$HL \xrightarrow{K_a} H^+ + L^- \quad (2)$$

where HL are the protonated binding sites on the surface and H^+ is the hydrogen concentration measured directly with a calibrated pH electrode. L^- is the deprotonated surface reactive site with a net negative charge. Consequently, the apparent proton dissociation constant can be expressed as:

$$K_a = \frac{[L^-][H^+]}{[HL]} \quad (3)$$

pK_a is defined as – $\log K_a$.

The Linear Programming Model (LPM) created by Martinez et al. (2002, 2004) and Martinez and Ferris (2001) can be used to rationalize experimental results in order to obtain the main parameters of surface equilibrium. This method also takes into account the intrinsic affinity constant. Each reactive group in the cell wall of the biosorbent would have a characteristic intrinsic affinity constant (Martinez et al. 2002). This method allows minimizing the number of binding sites and the absolute error, rather than the least squats. However, LPM is a mathematical solution without any base in chemistry. In the case of surface acid–base titrations, a matrix is constructed by considering the experimental net surface charge excess ($b_{meas,i}$) for the ith addition of titrant expressed as:

$$b_{meas,i} = C_{bi} - C_{ai} + \left[H^+\right]_i - \left[OH^-\right]_i \quad (4)$$

C_{ai} and C_{bi} are the acid–base concentrations at the *ith* addition of titrant. Finally, the calculated net surface charge excess can be written as follows:

$$b_{calc,i} = \sum_{j=1}^{m} \left(\frac{[L_T]_j K_{a,j}}{K_{a,j} + [H^+]_i} + S_0 \right) \quad (5)$$

Here, m corresponds to the number of binding sites and $[L_T]$ with the site density. $K_{a,j}$ is the apparent acidity constant for the jth site, and S_0 is a constant which is necessary in order to account for positive changes on the surface (Brassard et al. 1990; Smith and Ferris 2001).

Cation-exchange capacity determined by acid–base titration is correlated with bioadsorption capacity evaluated via adsorption experiments. For example, if pH is higher than pK_a, functional groups suffer deprotonation and become available for metal ion interactions (Ofomaja and Ho 2007). The concentration of functional groups computed via titration is responsible for the heavy metal adsorption on the cell surfaces. Generally these functional groups on the cell wall, tentatively ranked according with the pK_a value, are carboxyl, sulfonate, phosphoryl, amino, polyphenols amide, imidazole (González-Dávila 1995; González-Dávila et al. 1995; González et al. 2010; González and Pokrovsky 2014; Volesky et al. 1999; Pokrovsky et al. 2008a). These groups are ranked according to with the pK_a value

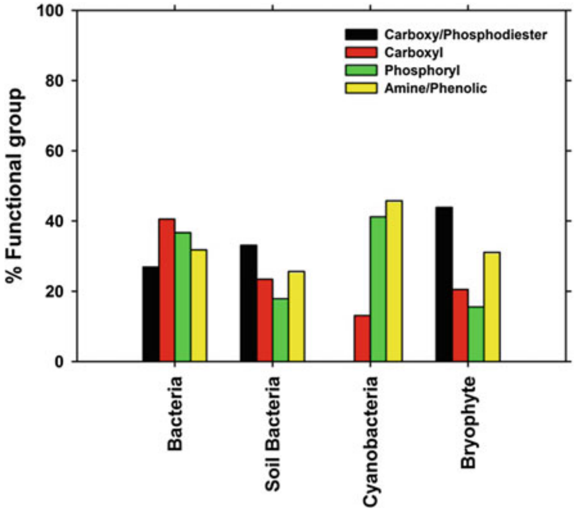

Fig. 1 Percentage of functional groups calculated via acid–base titration for different biosorbents as bacteria consortia (Borrok and Fein 2004), soil bacteria (González et al. 2010; Ueshima et al. 2008), cyanobacteria (Pokrovsky et al. 2008a; Martinez et al. 2008) and bryophytes (González and Pokrovsky 2014; González et al. 2016c)

computed from the acid–base titration. Figure 1 shows the concentration of functional groups for different biosorbents.

The composition of cell walls is very similar for most of the biosorbents, but small differences (in %) can have important effects in terms of bioadsorption. Biosorbents with high levels of carboxyl and hydroxyl groups are good sorbents, among them brown and green algae (Davis et al. 2003; Vieira and Volesky 2000), bacteria (Yee and Fein 2001) and bryophytes (González and Pokrovsky 2014). Gram-negative bacteria contain peptidoglycan and gram positive also teichoic acids (phosphoryl and hydroxyl groups). On the other hand, lower amounts of these groups and high levels of carrageen and sulfonate groups make them a less interesting biosorbent, for instance, red algae (Vieira and Volesky 2000).

Acid–base titrations also give us the pH values of the zero net proton adsorption (pH_{PZC}). This pH_{PZC} is directly linked to the chemical composition of the cell wall, and its variations between species can be understood in terms of its concentration of functional groups (Stumm and Morgan 1981; González-Dávila 1995; González-Dávila et al. 1995).

The chemical composition of the cell wall can also be studied with other techniques: IR, Raman, electron dispersive spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), electron microscopy (Scanning, Transmission), nuclear magnetic resonance (NMR), X-ray diffraction analysis and X-ray absorption spectroscopy (XAS) (Tsezos et al. 1997; Chojnacka 2010).

Particularly, the most interesting technique is XAS, including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure region (EXAFS). It is the most powerful microscopic technique for the quantitative construction of the molecular environment, both organically and inorganically, of heavy metals bioadsorbed on the cell surfaces (Pokrovsky et al. 2012; González et al. 2016a).

2.2 Kinetics of Bioadsorption

The kinetics of bioadsorption gives us useful information for understanding the adsorption rate of heavy metal onto the cell surfaces and the necessary time for a full absorption process (Santana-Casiano et al. 1995). In fact, kinetic studies are necessary to select ideal conditions for adsorption experiments (Tuzen and Sarı 2010). In addition, this kind of experiments allows us to understand the reaction pathways and mechanisms of adsorption (Gupta and Bhattacharyya 2011). Bioadsorption is a quick process and normally the equilibrium is reached in the first few minutes (González-Dávila et al. 1995; González and Pokrovsky 2014). This means that the kinetic experiments should be carried out carefully in order to be able to fit an adequate kinetic model. The reaction order is related to the mechanisms of bioadsorption, mainly ion exchange or surface precipitation (metal hydroxide, sulphide or carbonate).

Different kinetic models have been applied to biosorbents, including pseudo-first and second order, considering non-equilibrium conditions (Xu et al. 2004; Ho et al. 2000; Erdem and Ozverdi 2006; Kiran et al. 2006; Rubín et al. 2006; Won et al. 2006; Kumar et al. 2005).

2.2.1 Pseudo-first order kinetic model

Also known as Lagergren model, it assumes that metal ions are bound only to one binding site on the cell surface (Ghaedi et al. 2013; Chojnacka 2010). The kinetic rate is proportional to the number of free binding sites (Ghaedi et al. 2013) and can be written as:

$$\frac{\partial [Me^{2+}]_t}{\partial t} = k_1' \left([Me^{2+}]_e - [Me^{2+}]_t \right) \tag{6}$$

$[Me^{2+}]_e$ is the concentration of metal adsorbed at equilibrium, $[Me^{2+}]_t$ is the concentration of metal adsorbed at time t and k_1' (min^{-1}) is the pseudo-first adsorption rate constant. This adsorption rate constant and $[Me^{2+}]_e$ can be computed experimentally from the slope and intercept of the linear plot of ln ($[Me^{2+}]_e - [Me^{2+}]_t$) versus time ($min^{-1}$).

2.2.2 Second-order kinetic model

Second-order kinetic equation (Blanchard et al. 1984) in terms of adsorption has been used frequently (Ho et al. 2000). This model assumes that the rate-limiting step is most likely to involve chemical interactions leading to binding of the ions to the surface by bonding as strong as covalent bonding (Gupta and Bhattacharyya 2011). This model can be expressed as Chojnacka (2010):

$$\frac{\partial[Me^{2+}]_t}{\partial t} = k_2\left(\left[Me^{2+}\right]_e - \left[Me^{2+}\right]_t\right)^2 \qquad (7)$$

where k_2 (g mg^{-1} min^{-1}) is the second-order adsorption rate constant. Experimentally, the plot of (t/[Me^{2+}]$_t$) versus time (min^{-1}) results in 1//[Me^{2+}]$_t$ = slope and $1/k_2$[Me^{2+}]$_e$ = the intercept.

The pseudo-first kinetic model has been applied to the adsorption of Cd(II) onto *Hypnea valentiae* and *Mastocarpus stellatus* (Rathinam et al. 2010; Herrero et al. 2011). The second-order rate constant model has been applied to the adsorption of Cu(II), Cd(II), Pb(II) and Ni(II) on algae such as: *Ulva fasciata*, *Sargassum* sp. (Karthikeyan et al. 2007), *Laminaria*, *Durvillaea*, *Eckloniaand*, *Homostra* (Figueira et al. 2000), *Bifurcaria bifurcate*, *Saccorhiza polyschides*, *Ascophyllum nodosum*, *Laminaria ochroleuca*, *Pelvetia caniculate* (Lodeiro et al. 2005), *Oedogonium* sp. (Gupta and Rastogi 2008), *Fucus vesiculosus* (Mata et al. 2008), *Cystoseira indica*, *Nizmuddinia zanardini*, *Sargassum glaucescens* and *Padina australis* (Pahlavanzadeh et al. 2010).

2.3 Bioadsorption as a Function of pH

The effect of pH in terms of bioadsorption is based on the binding of metals onto the cell surfaces due to the negatively charged functional groups that form the cell wall. Despite the number of biosorbents, the composition of their cell walls is, as indicated above, very similar. Several authors (Yee and Fein 2001; Fein et al. 2001; Borrok and Fein 2004; González et al. 2010) proposed the principle of ‘‘*universal adsorption-edge*’’ developed earlier for heterotrophic bacteria and their consortia and soil bacteria and later used for the bioadsorption capacities of bryophytes (mosses; González and Pokrovsky (2014)). The adsorption of metal cations on the cell surface increases with the pH (Fig. 2), as the available sites to bind metals are fully protonated at low pH. However, this mechanism is only valid for cations (Naja and Volesky 2010). Another explanation considers that pH has a key control over the solubility of heavy metals in solution because it reduces the concentration of OH$^-$ and $CO_3{}^{2-}$ (Millero et al. 2009).

According to with the LPM (Martinez and Ferris 2001; Martinez et al. 2002; Martinez et al. 2004; Pokrovsky et al. 2008a; González et al. 2010), the pH-edge can be expressed, within this formalism by $K_{s,j}$, as the reaction between metal in solution and available surface sites:

$$Me^{2+} + B_jH^0 \xrightarrow{K_{s,j}} MeB_j^+ + H^+ \qquad (8)$$

B_j represents a surface reactive site and $K_{s,j}$ is the apparent concentration equilibrium constant conditional on ionic strength. For a jth deprotonated binding sites at the ith pH values, $K_{s,j}$ is as follows:

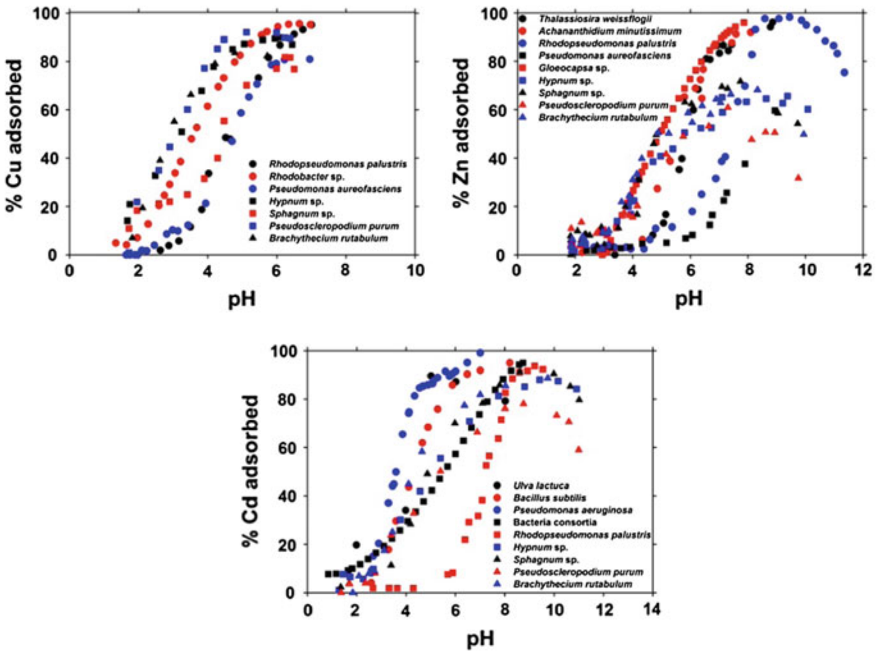

Fig. 2 Adsorption of Cu(II), Zn(II) and Cd(II) on several biosorbents. *Rhodopseudomonas palustris* (4 g L^{-1}; Pokrovsky et al. (2008b)); *Rhodobacter* sp. (4 g L^{-1}; Pokrovsky et al. (2008b)), *Pseudomonas aureofasciens* (4 g L^{-1}; González et al. (2010); Drozdova et al. (2014)); *Hypnum* sp., *Sphagnum* sp., *Pseudoscleropodium purum* and *Brachythecium rutabulum* (1 g L^{-1}; González and Pokrovsky (2014)), *Thalassiosira weissflogii*, *Achananthidium minutissimum* (35 and 25 g L^{-1}; Gelabert et al. (2006)), *Ulva lactuca* (20 g L^{-1}; Sarı and Tuzen (2008)), *Bacillus subtilis* (1 g L^{-1}; Fowle and Fein (2000)); Bacteria consortia (1 g L^{-1}; Borrok and Fein (2004)), *Gloeocapsa* sp. (4 g L^{-1}; Pokrovsky et al. (2008a)), *Pseudomonas aeruginosa* (1 g L^{-1}; Yee and Fein (2001))

$$K_{s,j} = \frac{[MeB_j^+]_i[H^+]_{meas,i}}{[Me^{2+}]_{meas,i}[B_jH^0]_i} \tag{9}$$

where $K_{s,j}$ is a function of experimentally determined proton and metal concentration ($[H^+]_{meas,i}$ and $[Me^{2+}]_{meas,i}$) and the amount of Me^{2+} bound to the jth site at the ith pH value ($[MeB_j^+]_i$).

Figure 2 shows the bioadsorption of Cu(II), Zn(II) and Cd(II) on different biosorbents such as bacteria, marine microalgae, algae, soil bacteria and bryophytes. This wide comparison demonstrates that the universal bio-surface pH-edge occurs for different organisms, probably only due to the composition of the cell wall. Bryophytes and bacteria are the most interesting biosorbents, capable of adsorbing the same amount of metal at a factor of 4–35 lower biomass concentration compared to other sorbents.

2.4 Bioadsorption as a Function of Metal Concentration in Solution

The bioadsorption capacity of a specific biosorbent can be studied as a function of metal cations in solution. The most common bioadsorption equilibrium isotherms are the Langmuir isotherms or Freundlich isotherms, but there are also other types of isotherm as described below.

2.4.1 Langmuir Isotherm

This isotherm has a surface with homogeneous binding sites. A monolayer adsorption occurs on the surface, equivalent adsorption energy and no interaction between adsorbed species (Langmuir 1918; Gupta and Rastogi 2008). In addition, when the binding sites are saturated, no more metal can be adsorbed to these sites. Accordingly, with increasing metal concentration, the surface will reach a saturation point at which the maximum adsorption capacity is achieved (Farhan et al. 2013). The Langmuir isotherm can be expressed as:

$$\frac{[Me^{2+}]_{aq}}{[Me^{2+}]_{ads}} = \frac{1}{K_L q_{max}} + \frac{[Me^{2+}]_{aq}}{q_{max}} \tag{10}$$

$[Me^{2+}]_{aq}$ (mgL^{-1}) is the concentration of aqueous metal, $[Me^{2+}]_{ads}$ ($mg\ g^{-1}$) is the concentration of metal adsorbed onto the biosorbent, K_L is the Langmuir constant related to the energy of adsorption and q_{max} is the maximum adsorption capacity. The q_{max} ($mg\ g^{-1}$) and K_L (Lmg^{-1}) can be determined from the linearization via $[Me^{2+}]_{aq}/[Me^{2+}]_{ads}$ versus $[Me^{2+}]_{aq}$.

2.4.2 Freundlich Isotherm

The Freundlich isotherm considers adsorption on heterogeneous surfaces with the interaction between adsorbed metals (Freundlich 1906). The Freundlich isotherm can be expressed as:

$$\log[Me^{2+}]_{ads} = \log k_F + \left(\frac{1}{n}\right) \log[Me^{2+}]_{aq} \tag{11}$$

where k_F and n are Freundlich constants characteristic of each biosorbent that give us information about the adsorption capacity and adsorption intensity, respectively. When $n = 1$, the adsorption is linear, when $n < 1$ the adsorption is a chemical process, and when $n > 1$, the adsorption is a physical process (Farhan et al. 2013). This equation is exponential and should only be used in the low to intermediate concentration ranges. The Freundlich equilibrium constants can be computed graphically from the plot of log $[Me^{2+}]_{ads}$ versus log $[Me^{2+}]_{aq}$.

2.4.3 Sips Isotherm

Sips (1948) proposed an empirical isotherm equation:

$$[Me^{2+}]_{aq} = \frac{K_s[Me^{2+}]_{ads}^{ns}}{1 + a_s[Me^{2+}]_{ads}^{ns}} \tag{12}$$

where K_s is the Sips constant (L mg^{-1}), a_s is the affinity coefficient (L mg^{-1}) and n_s is the heterogeneity coefficient.

2.4.4 Redlich–Peterson Isotherm

The Redlich–Peterson isotherm (Redlich and Peterson 1959) incorporates 3 parameters enabling its application in homogeneous and heterogeneous systems (Redlich and Peterson 1959; Padmavathy 2008). This isotherm can be expressed as:

$$\ln\left[\left(\frac{A[Me^{2+}]_{aq}}{[Me^{2+}]_{ads}}\right) - 1\right] = g\ln[Me^{2+}]_{aq} + \ln B \tag{13}$$

A, B and g ($0 < g < 1$) are the three isotherm constants. This isotherm will be the Freundlich isotherm when the concentration of aqueous metal is high. When $g = 1$, the Redlich–Peterson isotherm is equal to the Langmuir isotherm.

2.4.5 Tóth Isotherm

Toth (1971) suggested this isotherm, deriving it from the potential theory. It is applied for bioadsorption on heterogeneous biosorbents. This isotherm can be expressed as follows:

$$[Me^{2+}]_{ads} = q_{max}\frac{b_T[Me^{2+}]_{aq}}{\left[1 + (b_T[Me^{2+}]_{aq})^{1/n_T}\right]^{n_T}} \tag{14}$$

b_T and n_T are constants. This isotherm is reduced to the Langmuir isotherm when $n_T = 1$.

2.4.6 Frumkin Isotherm

The Frumkin isotherm takes the possible interaction between the bioadsorbed species into account (Grchev et al. 1991). This isotherm is expressed as a linear equation according to:

$$ln\left[\left(\frac{[Me^{2+}]_{ads}}{Q_F-[Me^{2+}]_{ads}}\right)\frac{1}{[Me^{2+}]_{aq}}\right] = \ln K_F + 2f\frac{[Me^{2+}]_{ads}}{Q_F} \tag{15}$$

where Q_F is the theoretical monolayer saturation capacity, f is the interaction coefficient and K_F is the equilibrium constant. This expression can be reduced to the Langmuir isotherm when $f = 0$.

2.4.7 Temkin Isotherm

Temkin and Pyzhev (1940) proposed this isotherm assuming an equal distribution of binding energies over the different binding sites on the surface of the biosorbent, and assuming that the heat of adsorption decreases linearly with the increase of the adsorbent. The linear form of the Temkin isotherm is:

$$[Me^{2+}]_{ads} = \frac{RT}{b}\ln\left(A[Me^{2+}]_{aq}\right) \tag{16}$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (Kelvin) and B the heat of adsorption. A is the equilibrium binding constant or Temkin isotherm constant.

As we mentioned before, the mathematical approach LPM (Martinez and Ferris 2001; Martinez et al. 2002, 2004) has been extensively used in order to fit the metal

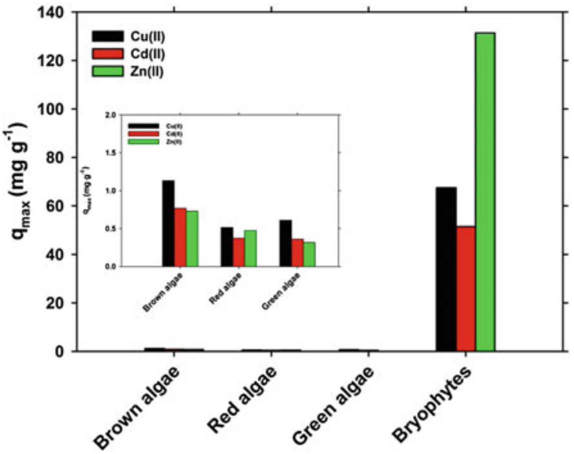

Fig. 3 Maximum adsorption capacity (q_{max}) for brown, green and red algae (see references in Table 1)

Table 1 Maximum adsorption capacity (q_{max}) measured via adsorption of metal ions onto cell surfaces for several biosorbents, at constant pH. Modified from He and Chen (2014)

Brown Algae				
Metal ions	Species	pH	q_{max} (mg g^{-1})	References
Pb(II)	*Ascophyllum nodosum*	3.5	1.31	Holan and Volesky (1994)
	Ascophyllum nodosum	3.0	0.86	Romera et al. (2007)
	Fucus spiralis	3.0	0.98	Romera et al. (2007)
	Fucus vesiculosus	3.5	1.11	Holan and Volesky (1994)
	Fucus vesiculosus	5.0	1.02	Mata et al. (2008)
	Padina pavonia	4.5	1.04	Jalali et al. (2002)
	Padina sp.	5.0	1.25	Sheng et al. (2004)
	Sargassum hystrix	4.5	1.37	Jalali et al. (2002)
	Sargassum natans	3.5	1.22	Holan and Volesky (1994)
	Sargassum natans	4.5	1.14	Jalali et al. (2002)
	Sargassum sp.	5.0	1.16	Sheng et al. (2004)
	Sargassum vulgare	3.5	1.10	Holan and Volesky (1994)
Cu(II)	*Ascophyllum nodosum*	4.0	0.91	Romera et al. (2007)
	Fucus serratus	5.5	1.60	Ahmady-Asbchin et al. (2008)
	Fucus spiralis	4.0	1.10	Romera et al. (2007)
	Fucus vesiculosus	5.0	1.66	Mata et al. (2008)
	Padina sp.	5.0	1.14	Sheng et al. (2004)
	Sargassum filipendula	4.5	0.89	Davis et al. (2000)
		4.5	1.32	Kleinübing et al. (2011)
	Sargassum fluitans	4.5	0.80	Davis et al. (2000)
	Sargassum sp.	5.0	0.99	Sheng et al. (2004)
		5.5	1.13	Karthikeyan et al. (2007)
	Sargassum vulgarie	4.5	0.93	Davis et al. (2000)
Cd(II)	*Ascophyllum nodosum*	6.0	0.78	Romera et al. (2007)
		4.5	0.70	Lodeiro et al. (2005)
	Bifurcaria bifurcate	4.5	0.65	Lodeiro et al. (2005)
	Fucus spiralis	6.0	1.02	Romera et al. (2007)
	Fucus vesiculosus	6.0	0.96	Mata et al. (2008)
	Laminaria ochroleuca	4.5	0.56	Lodeiro et al. (2005)
	Macrocystis pyrifera	3.0	0.89	Cazón et al. (2012)
	Padina sp.	5.5	0.75	Sheng et al. (2004)
	Padina tetrastomatica	5.0	0.53	Hashim and Chu (2004)
	Pelvetia caniculata	4.5	0.66	Lodeiro et al. (2005)
	Saccorhiza polyschides	4.5	0.84	Lodeiro et al. (2005)
	Sargassum baccularia	5.0	0.74	Hashim and Chu (2004)
	Sargassum filipendula	4.5	0.66	Davis et al. (2000)
		5.0	1.17	Luna et al. (2010)

(continued)

Table 1 (continued)

Brown Algae

Metal ions	Species	pH	q_{max} (mg g^{-1})	References
	Sargassum fluitans	4.5	0.71	Davis et al. (2000)
	Sargassum muticum	4.5	0.68	Davis et al. (2000)
	Sargassum siliquosum	5.0	0.73	Hashim and Chu (2004)
	Sargassum sp.	4.5	0.78	Davis et al. (2000)
		5.5	0.76	Sheng et al. (2004)
	Sargassum vulgarie	4.5	0.79	Davis et al. (2000)
Zn(II)	*Ascophyllum nodosum*	6.0	0.64	Romera et al. (2007)
	Fucus spiralis	6.0	0.81	Romera et al. (2007)
	Macrocystis pyrifera	4.0	0.91	Cazón et al. (2012)
	Padina sp.	5.5	0.81	Sheng et al. (2004)
	Sargassum filipendula	5.0	0.71	Luna et al. (2010)
	Sargassum sp.	5.5	0.50	Sheng et al. (2004)
Ni(II)	*Ascophyllum nodosum*	3.5	0.69	Holan and Volesky (1994)
	Ascophyllum nodosum	6.0	0.73	Romera et al. (2007)
	Cystoseria indica	6.0	0.85	Pahlavanzadeh et al. (2010)
	Fucus spiralis	6.0	0.85	Romera et al. (2007)
	Fucus vesiculosus	3.5	0.39	Holan and Volesky (1994)
	Nizmuddinia zanardini	6.0	0.94	Pahlavanzadeh et al. (2010)
	Padina australis	6.0	0.46	Pahlavanzadeh et al. (2010)
	Padina sp.	5.5	0.63	Sheng et al. (2004)
	Sargassum filipendula	4.5	1.07	Kleinübing et al. (2011)
	Sargassum fluitans	3.5	0.75	Holan and Volesky (1994)
	Sargassum glaucescensand	6.0	0.94	Pahlavanzadeh et al. (2010)
	Sargassum natans	3.5	0.41	Holan and Volesky (1994)
	Sargassum sp.	5.5	0.61	Sheng et al. (2004)
	Sargassum vulgare	3.5	0.09	Holan and Volesky (1994)

Green algae

Metal ions	Species	pH	q_{max} (mg g^{-1})	References
Pb(II)	*Caulerpa lentillifera*	5.0	0.13	Kleinübing et al. (2011)
	Cladophora glomerata	4.5	0.35	Jalali et al. (2002)
	Cladophora sp.	5.0	0.22	Lee and Chang (2011)
	Codium vermilara	5.0	0.30	Romera et al. (2007)
	Spirogyra insignis	5.0	0.24	Romera et al. (2007)
	Spirogyra neglecta	5.0	0.56	Singh et al. (2007)
	Spirogyra sp.	5.0	0.43	Lee and Chang (2011)
	Ulva lactuca	4.5	0.61	Jalali et al. (2002)
	Ulva sp.	5.0	1.46	Sheng et al. (2004)

(continued)

Table 1 (continued)

Brown Algae				
Metal ions	Species	pH	q_{max} (mg g^{-1})	References
Cu(II)	*Caulerpa lentillifera*	5.0	0.08	Pavasant et al. (2006)
	Cladophora sp.	5.0	0.23	Lee and Chang (2011)
	Codium vermilara	5.0	0.26	Romera et al. (2007)
	Spirogyra insignis	4.0	0.30	Romera et al. (2007)
	Spirogyra neglecta	4.5	1.80	Singh et al. (2007)
	Spirogyra sp.	5.0	0.60	Lee and Chang (2011)
	Spirogyra sp.	5.0	0.53	Rajfur et al. (2012)
	Ulva fasciata	5.5	1.14	Karthikeyan et al. (2007)
	Ulva fasciata	5.0	0.42	Karthikeyan et al. (2007)
	Ulva sp.	5.0	0.75	Sheng et al. (2004)
Cd(II)	*Caulerpa lentillifera*	5.0	0.04	Pavasant et al. (2006)
	Chaetomorpha linum	5.0	0.48	Hashim and Chu (2004)
	Codium vermilara	6.0	0.19	Romera et al. (2007)
	Oedogonium sp.	5.0	0.79	Gupta and Rastogi (2008)
	Spirogyra insignis	6.0	0.20	Romera et al. (2007)
	Ulva lactuca	5.0	0.25	Sarı and Tuzen (2008)
	Ulva sp.	5.5	0.58	Sheng et al. (2004)
Zn(II)	*Caulerpa lentillifera*	5.0	0.04	Pavasant et al. (2006)
	Codium vermilara	6.0	0.36	Romera et al. (2007)
	Spirogyra insignis	6.0	0.32	Romera et al. (2007)
	Ulva sp.	5.5	0.54	Sheng et al. (2004)
Ni(II)	*Codium vermilara*	6.0	0.22	Romera et al. (2007)
	Spirogyra insignis	6.0	0.29	Romera et al. (2007)
	Ulva lactuca	4.5	1.14	Zakhama et al. (2011)
	Ulva sp.	5.5	0.29	Sheng et al. (2004)
Red algae				
Metal ions	Species	pH	q_{max} (mg g^{-1})	References
Pb(II)	*Asparagopsis armata*	4.0	0.30	Romera et al. (2007)
	Chondrus crispus	4.0	0.98	Romera et al. (2007)
	Corallina mediterranea	5.0	0.31	Ibrahim (2011)
	Galaxaura oblongata	5.0	0.42	Ibrahim (2011)
	Gracilaria canaliculata	4.5	0.20	Jalali et al. (2002)
	Gracilaria corticata	4.5	0.26	Jalali et al. (2002)
	Gracillaria sp.	5.0	0.45	Sheng et al. (2004)
	Jania rubens	5.0	0.14	Ibrahim (2011)
	Polysiphonia violacea	4.5	0.49	Jalali et al. (2002)
	Pterocladia capillacea	5.0	0.16	Ibrahim (2011)

(continued)

Table 1 (continued)

Brown Algae

Metal ions	Species	pH	q_{max} (mg g^{-1})	References
Cu(II)	*Asparagopsis armata*	5.0	0.33	Romera et al. (2007)
	Chondrus crispus	4.0	0.63	Romera et al. (2007)
	Gelidium sp.	5.3	0.51	Vilar et al. (2008)
	Gracillaria sp.	5.0	0.59	Sheng et al. (2004)
Cd(II)	*Asparagopsis armata*	6.0	0.28	Romera et al. (2007)
	Ceramium virgatum	5.0	0.35	Sarı and Tuzen (2008)
	Chondrus crispus	6.0	0.66	Romera et al. (2007)
	Corallina mediterranea	5.0	0.57	Ibrahim (2011)
	Galaxaura oblongata	5.0	0.76	Ibrahim (2011)
	Gracilaria changii	5.0	0.23	Hashim and Chu (2004)
	Gracilaria edulis	5.0	0.24	Hashim and Chu (2004)
	Gracilaria salicornia	5.0	0.16	Hashim and Chu (2004)
	Gracillaria sp.	5.5	0.30	Sheng et al. (2004)
	Hypnea valentiae	6.0	0.15	Rathinam et al. (2010)
	Jania rubens	5.0	0.27	Ibrahim (2011)
	Mastocarpus stellatus	6.0	0.59	Herrero et al. (2011)
	Pterocladia capillacea	5.0	0.29	Ibrahim (2011)
Zn(II)	*Asparagopsis armata*	6.0	0.33	Romera et al. (2007)
	Chondrus crispus	6.0	0.69	Romera et al. (2007)
	Gracillaria sp.	5.5	0.40	Sheng et al. (2004)
Ni(II)	*Asparagopsis armata*	6.0	0.29	Romera et al. (2007)
	Chondrus crispus	6.0	0.63	Sheng et al. (2004)
	Gracillaria sp.	5.5	0.28	Sheng et al. (2004)

Others (Microalgae, Soil bacteria, Bacteria, Bryophytes)

Metal ions	Species	pH	q_{max} (mg g^{-1})	References
Pb(II)	*Australian Marine algae DP95Ca*	5.0	320.85	Matheickal and Yu (1999)
	Australian Marine algae ER95Ca	5.0	260.82	Matheickal and Yu (1999)
	Bacillus cereus	5.5	36.71	Pan et al. (2007)
	Rhodococcus opacus	5.0	94.19	Bueno et al. (2008)
	Hypnum sp.	6.5	312.66	González and Pokrovsky (2014)
	Sphagnum sp.	6.5	229.78	González and Pokrovsky (2014)
	Pseudoscleropodium purum	6.5	182.34	González and Pokrovsky (2014)
	Brachythecium rutabulum	6.5	530.43	González and Pokrovsky (2014)

(continued)

Table 1 (continued)

Brown Algae				
Metal ions	Species	pH	q_{max} (mg g^{-1})	References
Cu(II)	*Australian Marine algae DP95Ca*	5.0	82.55	Matheickal and Yu (1999)
	Australian Marine algae ER95Ca	5.0	70.49	Matheickal and Yu (1999)
	Bacillus cereus	5.5	50.32	Pan et al. (2007)
	Hypnum sp.	5.5	63.16	González and Pokrovsky (2014)
	Sphagnum sp.	5.5	81.85	González and Pokrovsky (2014)
	Pseudoscleropodium purum	5.5	86.17	González and Pokrovsky (2014)
	Brachythecium rutabulum	5.5	49.69	González and Pokrovsky (2014)
	Sphagnum denticulatum	5.5	79.44	González et al. (2016c)
	Sphagnum palustre	5.5	42.58	González et al. (2016b)
		5.5	69.27	González et al. (2016b)
Cd(II)	*Hypnum* sp.	6.5	35.75	González and Pokrovsky (2014)
	Sphagnum sp.	6.5	81.95	González and Pokrovsky (2014)
	Pseudoscleropodium purum	6.5	29.56	González and Pokrovsky (2014)
	Brachythecium rutabulum	6.5	51.26	González and Pokrovsky (2014)
Zn(II)	*Achananthidium minutissimum*	6.2	0.36	Gelabert et al. (2006)
	Hypnum sp.	6.8	45.90	González and Pokrovsky (2014)
	Sphagnum sp.	6.8	60.74	González and Pokrovsky (2014)
	Pseudoscleropodium purum	6.8	58.91	González and Pokrovsky (2014)
	Brachythecium rutabulum	6.8	68.58	González and Pokrovsky (2014)
	Skeletonema costatum	7.2	2.62	Gelabert et al. (2006)
	Sphagnum denticulatum	6.5	60.80	González et al. (2016c)
	Sphagnum palustre	6.5	253.02	González et al. (2016c)
		6.5	300.75	González et al. (2016c)
	Thalassiosira weissflogii	7.5	0.131	Gelabert et al. (2006)
Ni(II)	*Chlorella vulgaris*	4.5	86.60	Aksu and Dönmez (2006)
	Hypnum sp.	5.6	5.22	González and Pokrovsky (2014)

(continued)

Table 1 (continued)

Brown Algae				
Metal ions	Species	pH	q_{max} (mg g^{-1})	References
	Sphagnum sp.	5.6	6.28	González and Pokrovsky (2014)
	Pseudoscleropodium purum	5.6	3.64	González and Pokrovsky (2014)
	Brachythecium rutabulum	5.6	4.17	González and Pokrovsky (2014)

adsorbed onto the cell wall at fixed pH (González et al. 2010; González and Pokrovsky 2014; González et al. 2016c; Pokrovsky et al. 2008a). In this sense, in the case of the Langmuir isotherm adsorption (at fixed pH) the reaction between metal and binding sites can be expressed as:

$$Me^{2+} + B_j^- \xrightarrow{K_{m,j}} MeB_j^+ \tag{17}$$

where B_j is the specific surface functional group and $K_{m,j}$ is the apparent metal-ligand binding constant conditional on ionic strength. At *jth* deprotonated functional group and fixed pH value is written as follows:

$$K_{m,j} = \frac{\left[MeB_j^+\right]}{[Me^{2+}]_{meas,\,i}[B_j]_i} \tag{18}$$

In addition, $K_{m,j}$ is a function of experimental metal concentration ($[Me^{2+}]_{meas,i}$) and of the amount of Me^{2+} bound to the *jth* site as a function of increasing biomass and at fixed pH value ($[MeB_j^+]_i$). In the same way as the above treatment, the available binding sites are computed and assigned to a fixed $pK_{m,j}$ grid.

Note that the values of $K_{s,j}$ and $K_{m,j}$ computed are not directly comparable because K_s is a function of K_m ($K_s = K_m \cdot K_a$), where K_a is the acidity constant for a specific functional group on the biosorbent surface.

Figure 3 represents the q_{max} (mg g^{-1}) for the most interesting groups of biosorbents (Table 1.). Bryophytes are able to adsorb > 60-fold Cu(II), > 50-fold Cd(II) and > 200-fold Zn(II) compared to brown, red and green algae, respectively. It is important to remark that the bryophytes here include natural and produced under laboratory conditions (González et al. 2016c). In this regard, the comparison of the biosorption capacity of algae, brown algae are the most interesting ones because of the composition of their cell wall, with high levels of carboxyl and hydroxyl functional groups (Davis et al. 2003; Vieira and Volesky 2000).

Table 1 represents a compilation of the biosorption capacities (q_{max}) of several biosorbents (algae, bacteria, soil bacteria and bryophytes).

3 Commercial Applications

Adsorption of heavy metals on biosorbents has been mainly investigated at laboratory scale, as can be concluded from the references cited in this chapter. Only a few companies and laboratories have been involved in transferring the bioadsorption to industrial scale. The future goes through this transformation and this is the only way to obtain satisfactory results to solve the problem of pollution with heavy metals, especially in water bodies.

The USA and Canada were the first countries to carry out bioadsorption processes at industrial scale, accepted by EPA (EPA/540/S5-90/005). The positive results obtained by these experiences motivated the scientists to continue, though timidly, the application at this level, although we need to improve our knowledge about bioadsorption processes and biosorbents to obtain satisfactory and long-term results. On the other hand, future research should address improving our knowledge about the adsorption capacity of biosorbents in multi-heavy metal solutions, as the metal interaction in solution can affect the redox chemistry of these metals (i.e. copper–iron interactions; González et al. (2016b) or this interaction can affect the binding capacity (González-Dávila et al. 1995; Bueno et al. 2008).

Different commercial biosorbents and their characteristics are presented here.

(a) **BIO-FIX** is commercialized by the US Bureau of Mines (Golden, Co, USA) to remove heavy metals during the wastewater treatment. Bio-fix is a porous polymeric bead produced with non-living biomaterial: peat moss, algae, biological polymers and other materials with high metal affinity (Jeffers et al. 1993). These beads have an excellent handling and they have been satisfactory used for Cu(II), Cd(II), Zn(II) and Pb(II). In addition, this material can be reused due to the high reversible characteristics after acid solution treatment.

(b) **AMT-BIOCLAIM** has been developed by Advanced Mineral Technologies, Inc. (AMT) via bacterial fermentation processes (Brierley 1985, 1990). They used *Bacillus subtilis* as main bacteria because it is one of the most studied bacteria in terms of bioadsorption. This material also presents high recovery rates of heavy metal, being ~99% for Ag, Cd, Cu, Pb and Zn.

(c) **ALGASORB™** was produced by Bio-Recovery System, Inc. (USA). It consists in Chlorella vulgaris immobilized in silica gel polymer matrix. It can be used for a wide range of heavy metal concentrations (1–100 mg g^{-1}). The material is immobilized in silica gel polymer for protection of the cells and to be able to form a sorbent that can be added in columns. ALGASORB™ can be reused after treatment with acid–base solutions to remove the adsorbed material.

(d) **BV-SORBEX™** is produced by BV Sorbex, Inc. (Montreal, Canada). This adsorbent contains powder and granules (0.1–3 mm) formed by algae (*Sphaerotilus natans, Ascophyllum nodosum, Halimeda opuntia, Palmyra pomata, Chondrus crispus, Chlorella vulgaris*) (Volesky 2003), and they are able to recover ~99% of metal in solution (available on the BV Sorbex website; http://www.bvsorbex.net).

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