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Biosorption of Metals: State of the Art, General Features, and Potential Applications for Environmental and Technological Processes

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1. Introduction

The interactions among cells and metals are present since the life origin, and they occur successfully in the nature. These interactions are performed on cellular envelope (walls and membranes) and in cellular interior. They are based on the adsorption and absorption of metals by cells for the production of biomolecules and in vital metabolic processes (Palmieri, 2001). Some metals such as calcium, cobalt, copper, iron, magnesium, manganese, nickel, potassium, sodium, and zinc are required as essential nutrients to life existence. The principal functions of metals are: the catalysis of biochemical reactions, the stabilization of protein structures, and the maintenance of osmotic balance. The transition metals as iron, copper, and nickel are involved in redox processes. Other metals as manganese and zinc stabilize several enzymes and DNA strands by electrostatic interactions. Iron, manganese, nickel, and cobalt are components of complex molecules with a diversity of functions. Sodium and potassium are required for the regulation of intracellular osmotic pressure (Bruins et al., 2000).

The interactions among metals and biomasses are performed through different mechanisms. For instance, on cellular envelope, the metal uptake occurs via adsorption, coordination, and precipitation due to the interaction among the surface chemical groups and metals in aqueous solution. Similar mechanisms are related in the exopolymeric substances (EPS). On the other hand, specific enzymes in some biomasses can change the oxidation state of the noxious metals followed by formation of volatile compounds, which removes the metal from aqueous solution. Finally, the life maintenance depends on the metal absorption by active transport according with the nutritional requirements of the biomass (Gadd, 2009; Palmieri, 2001; Sen & Sharadindra, 2009).

The removal of metallic ions of an aqueous solution from cellular systems is carried out by passive and/or active forms (Aksu, 2001; Modak & Natarajan, 1995). As such live cells as dead cells do interact with metallic species. The bioaccumulation term describes an active process that requires the metabolic activity of the organisms to capture ionic species. In the active process the organisms usually tend to present tolerance and/or resistance to metals when they are in high concentrations and/or they are not part of the nutrition (Godlewska-Zylkiewicz, 2006; Zouboulis et al., 2004).

Group	Occurrence	pKa
Carboxylate	Uronic acid	3-4.4
Sulfate	Cisteic acid	1.3
Fosphate	Polysaccharides	0.9-2.1
Imidazol	Hystidine	6-7
Hydroxyl	Tyrosine-phenolic	9.5-10.5
Amino	Cytidine	4.1
Imino	Peptides	13

Table 1. Some chemical groups involved in the metal-biomass interactions and their pK_as.
Source: Eccles, 1999.

Biosorption is a term that describes the metal removal by its passive linkage in live and dead biomasses from aqueous solutions in a mechanism that is not controlled by metabolic steps. The metal linkage is based on the chemical properties of the cellular envelope without to require biologic activity (Gadd, 2009; Godlewska-Zylkiewicz, 2006; Palmieri et al., 2000; Valdman et al., 2001; Volesky, 2001). The process occurs through interaction among the metals and some active sites (e.g. carboxylate, amine, sulfate, etc.) on cellular envelope. Some of these chemical groups and their respective pK_as are described in the Table 1.

2. Biosorption of metals: general features

Usually, metallic species are not biodegradable and they are removed physically or chemically from contaminated effluents (Ahluwalia & Goyal, 2007; Hashim & Chu, 2004; Tien, 2002). The biosorption is a bioremediation emerging tool for wastewater treatment that has gained attention in the scientific community in the last years (Chu, 2004). It is a promising biotechnological alternative to physicochemical classical techniques applied such as: chemical precipitation, electrochemical separation, membrane separation, reverse osmosis, ion-exchange or adsorption resins (Ahluwalia & Goyal, 2007; Deng & Bai, 2004; Vegliò et al., 2002; Vegliò et al., 2003; Zouboulis et al., 2004). The conventional methods (Table 2) involve or capital and operational high costs, or they are inefficient at low metal concentration (1-100 ppm), or they can be associated to production of secondary residues that present treatment problems (Aksu, 2001; Ahluwalia & Goyal, 2007).

The initial incentives of biosorption development for industrial process are: (a) low cost of biosorbents, (b) great efficiency for metal removal at low concentration, (c) potential for biosorbent regeneration and metal valorization, (d) high velocity of sorption and desorption, (e) limited generation of secondary residues, and (f) more environmental friendly life cycle of the material (easy to eliminate compared to conventional resins, for example) (Crini, 2005; Kratochvil & Volesky, 2000; Volesky & Naja, 2005). Therefore the use of dead biomasses is generally preferred since it limits the toxicity effects of heavy metals (which may accumulate at the surface of cell walls and/or in the cytoplasm) and the necessity to provide nutrients (Modak & Natarajan, 1995; Sheng et al., 2004; Volesky, 2006).

Methodology	Disadvantages	Advantages
Chemical precipitation	<ul style="list-style-type: none"> a. Hard separation; b. Generation of secondary residues; c. Commonly inefficient in low metal concentration 	<ul style="list-style-type: none"> a. Simple procedures; b. Generally presents low costs
Electrochemical treatment	<ul style="list-style-type: none"> a. Possibility of application in high metal concentration; b. Technique is sensible under determined conditions, as the presence of interfering agents 	<ul style="list-style-type: none"> a. Successful metal recuperation
Reverse osmosis	<ul style="list-style-type: none"> a. Application of high pressures; b. Membranes that can foul or peel; c. High costs 	<ul style="list-style-type: none"> a. Effluent purification that become available to recycle
Ion-exchange	<ul style="list-style-type: none"> a. It is sensible to the presence of particulate materials; b. Resins with high costs 	<ul style="list-style-type: none"> a. Effective; b. Possibility of metal recuperation
Adsorption	No efficiency for some metals	Conventional adsorbents (e.g. activated carbon and zeolites)

Table 2. Conventional methods of metal removal from aqueous systems. Source: Zouboulis et al., 2004.

The mechanisms involved in metal accumulation on biosorption sites are numerous and their interpretation is made difficult because the complexity of the biologic systems (presence of various reactive groups, interactions between the compounds, etc.) (Gadd, 2009; Godlewska-Zylkiewicz, 2006; Palmieri, 2001). However, in most cases, metal binding proceeds through electrostatic interaction, surface complexation, ion-exchange, and precipitation, which can occur individually or combined (Yu et al., 2007a; Zouboulis et al., 2004). The uptake of metallic ions starts with the ion diffusion to surface of the evaluated biomasses. Once the ion is diffused to cellular surface, it bonds to sites that display some affinity with the metallic species (Aksu, 2001).

In general, literature describes that the biosorption process takes in consideration: (a) the temperature does not influence the biosorption between 20 and 35 °C; (b) the pH is a very important variable on process, once it affects the metal chemical speciation, the activity of biomass functional groups (active sites), and the ion metallic competition by active sites; (c) in diluted solutions, the biomass concentration influences on biosorption capacity: in lower concentrations, there is an increase on biosorption capacity; and (d) in solutions with different metallic species there is the competition of distinct metals by active sites (Vegliò & Beolchini, 1997).

The biosorption performance is influenced by physicochemical parameters as: (a) the biomass nature: the physical structure (porosity, superficial area, particle size) and the chemical nature of functional groups (diversity and density); (b) the chemical and the availability of the adsorbate; and (c) the solution conditions, such as: ionic force, pH, temperature and adsorbate concentration (Gadd, 2009; Godlewska-Zylkiewicz, 2006; Crini, 2005).

3. Environmental and technological demands

Environmental demands have received a great focus in public policies of different world's nations in the last decades. This is resulted of the external pressures of distinct areas as such the media vehicles, the scientific researches, and the greater conscious of the civil society about the environmental topics (Karnitz Jr., 2007; Volesky, 2001). These pressures have intensified the creation of regulatory laws as the water control and handling from anthropogenic activities. The mining and metallurgy wastewaters are considered the big resources of heavy metals contamination (cadmium, chromium, mercury, lead, zinc, copper, etc.) that are noxious in low concentrations (Sen & Sharadindra, 2009). The heavy metal recuperation from industrial effluents is extremely important due the society current requirements by the metal recycling and conservation (Hashim & Chu, 2004). The need for economic and effective methods for heavy metals removal from aqueous systems has resulted in the development of new technologies of concentration and separation (Hashim & Chu, 2004; Karnitz Jr., 2007; Sen & Sharadindra, 2009).

The biosorption of metals is established as research area since the 80s. The literature is mainly associated to the bioremediation of industrial wastewaters with low metal concentration. These works have been focused in the uptake of heavy metals because the metal ions in the environment bioaccumulate and are biomagnified along the food chain (Ahluwalia & Goyal, 2007; Vegliò et al., 2003; Volesky, 2001).

Besides the studies on environmental field of biosorption processes, others applications were investigated in the last few years led to develop the recovery of high demand and/or aggregated value metals such as gold, silver, uranium, thorium, and recently rare earth metals (RE) (Palmieri, 2001). The selection of interest metals in order to apply biosorption processes for recovery have to consider: (a) the environmental risk based on the technologic uses and the market value; and (b) the depletion rate of the metal resources, which is used as an indicator of variations on metal prices (Zouboulis et al., 2004). The price variations of interesting metals are essentially related to the market demands, environmental legislation, and energetic costs (Diniz & Volesky, 2005).

4. Biosorbents

There is a great variety of biomasses used to achieve the biosorption of metals as such micro and macroalgae, yeasts, bacteria, crustacean, etc. The use of adsorbents from dead organisms has an attractive economic cost because they are originated in less expensive materials in comparison to the conventional technologies. Other economic advantage is the possibility of biosorbent reuse from agro-industrial and domestic wastes (e.g., fermentation processes in breweries and pharmaceuticals, activated sludge, sugarcane bagasse, etc.) (Godlewska-Zylkiewicz, 2006; Karnitz Jr., 2007; Pagnanelli et al. 2004; Palmieri et al., 2002).

Commonly, the biosorption studies describe applications with native biomasses and with products obtained from biomasses, which are generally biopolymers (polysaccharides and glycoproteins).

The use of biosorbents in native forms from microbial biomasses (e.g. yeasts, microalgae, bacteria, etc.) present a series of problems: the difficulty on separation of cells after the biosorption, the mass loss during the separation, and the low mechanic resistance of the cells (Arica et al., 2004; Sheng et al., 2008; Vegliò & Beolchini, 1997; Vullo et al., 2008). The biomass immobilization makes possible a material with more appropriated size, greater mechanic resistance, and desirable porosity to use in fixed-bed columns (Sheng et al., 2008; Zhou et al., 2005). Besides the immobilization provides the metal recuperation and the column reuse (Sheng et al., 2008; Zhou et al., 2005).

The most common immobilization procedures are: (a) the adsorption on inert supports by preparation of biofilms; (b) the encapsulation in polymeric matrices as calcium alginate, polyacrylamide, polysulfone, and polyhydroxyethylmetacrilate; (c) the covalent linkage on supports by chemical agents; and (d) the cross-linking by chemical agents that form stable cellular aggregated. The most common chemical agents used are formaldehyde, glutaraldehyde, divinylsulfone, and formaldehyde-urea mixture (Vegliò & Beolchini, 1997). An important area that has been developed is the surface modification of biomasses by the insertion of additional chemical groups to increase the biosorption uptake process (Yang & Chen, 2008; Yu et al., 2007a; Yu et al., 2007b). This procedure is used for biomasses with low uptake capacities and in numerous cases the chemical modification also provides the cellular immobilization.

Since the 80s several biosorption processes have been developed in commercial scale. Some commercial applications are described by Wang & Chen (2009):

- a. B. V. SORBEX Inc.: several biosorbents of different biomaterials from biomass as such *Sargassum natans*, *Acophylum nodosum*, *Halimeda opuntia*, *Palmira pamata*, *Chondrus crispus*, and *Chlorella vulgaris*, which can adsorb a broad range of metals and can be regenerated easily;
- b. Advance Mineral Technologies Inc.: biosorbents based in *Bacillus* sp., but that finished their operations in 1988;
- c. AlgaSORB (Bio-recovery Systems Inc.): biomass *Chlorella vulgaris* immobilized in silica and polyacrylamide gels that adsorb metals of diluted solution with concentrations between 1-100 mg/L and can undergo more than 100 biosorption-desorption cycles;
- d. AMT-BIOCLAIM™ (Visa Tech Ltd.): biosorbent from *Bacillus subtilis* immobilized in polyethyleneimine and glutaraldehyde beads, which removes efficiently metals as gold, cadmium, and zinc from cyanide solutions. The biosorbent is not selective, but it presents high metal recuperation (99%) and can be regenerated by sodium hydroxide or sulfuric acid solutions;
- e. BIO-FIX (U. S. Bureau of Mines): biosorbent based in several biomasses, including *Sphagnum* peat moss, yeast, bacteria, and/or aquatic flora immobilized in high density polysulfone. The biosorbent is selective for heavy metals and it is applied in acid mine drainages. The metals can be eluted more than 120 recycles with solutions of hydrochloric acid and nitric acid.

Additionally the Table 3 presents some biosorbents and their applications in biosorption purposes.

Metal	Biosorbent	Reference
Gd	Several microorganisms (fungal and bacteria) from sand	Andrès et al., 2000
Hg, Cd, and Zn	Ca-alginate and immobilized wood-rotting fungus <i>Funalia trogii</i>	Arica et al., 2004
Sm and Pr	<i>Sargassum</i> sp.	Oliveira et al., 2011
Cu	<i>Sargassum</i> sp. immobilized in poly(vinyl alcohol) cryogel beads	Sheng et al., 2008
Co and Ni	<i>Ulva reticulata</i> , <i>Turbinaria ornata</i> , <i>Sargassum ilicifolium</i> , <i>Sargassum wightii</i> , <i>Gracilaria edulis</i> , and <i>Geledium</i> sp.	Vijayaraghavan et al., 2005
Cd, Zn, and Pb	<i>Laminaria hyperborea</i> , <i>Bifurcaria bifurcata</i> , <i>Sargassum muticum</i> , and <i>Fucus spiralis</i>	Freitas et al., 2008
Cu and Pb	Activated sludge	Xuejiang et al., 2006
La, Nd, Eu, and Gd	<i>Sargassum</i> sp.	Oliveira & Garcia Jr., 2009
Pb and Zn	<i>Phanerochaete chrysosporium</i> immobilized in Ca-alginate	Arica et al., 2003
Pb	<i>Streptomyces rimosus</i>	Selatnia et al., 2004
Pb	Cellulose/chitin beads	Zhou et al., 2005
Ni	<i>Sargassum wightii</i>	Vijayaraghavan et al., 2006
Cr	<i>Sargassum</i> sp.: raw and chemically modified (treated with NaOH, HCl, CaCl ₂ , formaldehyde, or glutaraldehyde)	Yang & Chen, 2008
Cu	Sugarcane bagasse: raw and chemically modified (treated with NaOH and/or citric acid)	Dos Santos et al., 2011
Cu, Mo, and Cr	Chitosan: flakes, beads, and modified beads (treated with glutaraldehyde)	Dambies et al., 2000
Ag	<i>Lactobacillus</i> sp.	Lin et al., 2005
Cd, Cu, and Ni	Aerobic granules	Xu & Liu, 2008
Cr and V	Waste crab shells	Niu & Volesky, 2006
Cd and Pb	Modified baker's yeast (treated with glutaraldehyde and cystine)	Yu et al., 2007a
Eu	Alfafa	Parsons et al., 2002
Pb, Zn, Cd, Fe, La, and Ce	Cross-linked <i>Laminaria japonica</i> (treated with propanol and HCl)	Ghimire et al., 2008
U, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu	<i>Dictyota dichotoma</i> , <i>Ecklonia stolonifera</i> , <i>Undaria pinnatifida</i> , <i>Sargassum honeri</i> , and <i>Sargassum hemiphyllum</i>	Sakamoto et al., 2008

Table 3. Biosorbents used in some biosorption purposes.

5. Biosorption in batch systems

The quantitative information in the biosorption purposes can be obtained from equilibrium analysis on batch experiments (Volesky, 2003). In these experiments are assayed the optimal conditions to perform a more effective biosorption and they may be used in the research of physicochemical models that describe the metal-biomass interactions. Despite of the continuous operation in columns to be the preferential mode for amplifying the biosorption process to a pilot scale (Volesky, 2003), the batch systems serve as pre-stage for an initial evaluation of adsorption phenomena and operational conditions before the application of the process on continuous systems (Gadd, 2009). The main difference between the operational modes refers to transport phenomena involved: in batch systems the diffusive and convective resistances for the adsorption are pronouncedly diminished in relation to column systems, which exhibit smaller mass transfer rates due to dependence of the combination of several parameters.

The physicochemical modeling is based on the analysis of the metal uptake capacity (according with Eq. (1)) as function of the assay time (biosorption kinetics) or the equilibrium concentration of adsorbed metal (biosorption isotherms).

$$q = (C_0 - C_{EQ})V/M \quad (1)$$

where q is the metal uptake that represents the amount of accumulated metal by mass unity or matter moiety of biomass; V is the solution volume; C_0 e C_{EQ} are the initial and equilibrium concentrations (in the liquid phase), respectively; and M is the biomass mass.

Physicochemical models differ with regard to the number of adsorbed layers, the type of interactions among the active sites and metals, and the possibility to use the equilibrium constants among the solid and liquid phases. The criteria for choosing an isotherm or a kinetic equation for biosorption data is mainly based on the best adjustment of curve fitting which is often evaluated by statistical analysis. The model chosen should be the one reflecting the best the biosorption mechanisms (Liu & Liu, 2008; Vegliò et al., 2003). The next items exemplify the use of batch systems as much in the optimization of operational parameters as in the physicochemical modeling for the biosorption of metals.

5.1 Biosorption isotherms

The study of the phase equilibrium is a part of the thermodynamic that relate the equilibrium composition of two phases and it is represented by graphics of concentration in the stationary phase (expressed in biosorption purposes in terms of metal uptake, q) versus the concentration in the mobile phase, both at equilibrium (Godlewska-Zylkiewicz, 2006). Usually the mechanisms of adsorption and ion-exchange are the most used because their concepts are easily extended to other mechanisms of metal retention. The adsorption models in liquid-solid equilibrium are derived of models for gas-solid equilibrium from the Gibbs isotherm and assuming an equation of state for the adsorbed phase. The Table 4 displays some adsorption models used in biosorption studies and the advantages and disadvantage in their utilization.

These models (Table 4) differ in the amount of adsorbed layers, the interaction between the binding sites and the metal (adsorbent-adsorbate, adsorbate-adsorbate, and adsorbent-adsorbent), and the possibility to apply equilibrium constants equations between the liquid and solid phases. Obviously, these considerations for biosorption systems do not explain the

mechanisms of metal uptake due to the complexity of the biologic systems, but it supplies parameters that are utilized to evaluate the biosorption performance, such as the maximum metal uptake and the affinity of the active sites by metallic ions (Kratochvil & Volesky, 2000; Palmieri, 2001).

Biosorption of metals in the mostly cases of equilibrium isotherms is modeled according to non-linear functions that are described by Brunauer-Emmet-Teller (BET) type-I isotherms with hyperbolic shape (Guiochon et al., 2006). The general form of the curve $q = f(C_{EQ})$ is showed on Fig. 1.

Adsorption Model	Equation	Advantages	Disadvantages
Langmuir	$q = (q_{MAX}bC_{EQ})/(1+bC_{EQ})$	Interpretable parameters	Not structured; Monolayer Adsorption
Freundlich	$q = K_F C_{EQ}^{1/n}$	Simple expression	Not structured; No leveling off
Combination Langmuir-Freundlich	$q = (q_{MAX}bC_{EQ}^{1/n})/(1+bC_{EQ})$	Combination of above	Unnecessarily complicated
Radke-Prausnitz	$1/q = 1/(aC_{EQ}) + 1/(bC_{EQ}^{\beta})$	Simple expression	Empirical, uses 3 parameters
Brunauer-Emmet-Teller	$q = (BCQ^0)/\{[C_s - C][1 + (B-1)C/C_s]\}$	Multilayer adsorption; Inflection point	No total capacity equivalent

Table 4. Examples of physicochemical models of adsorption. Source: Volesky, 2003.

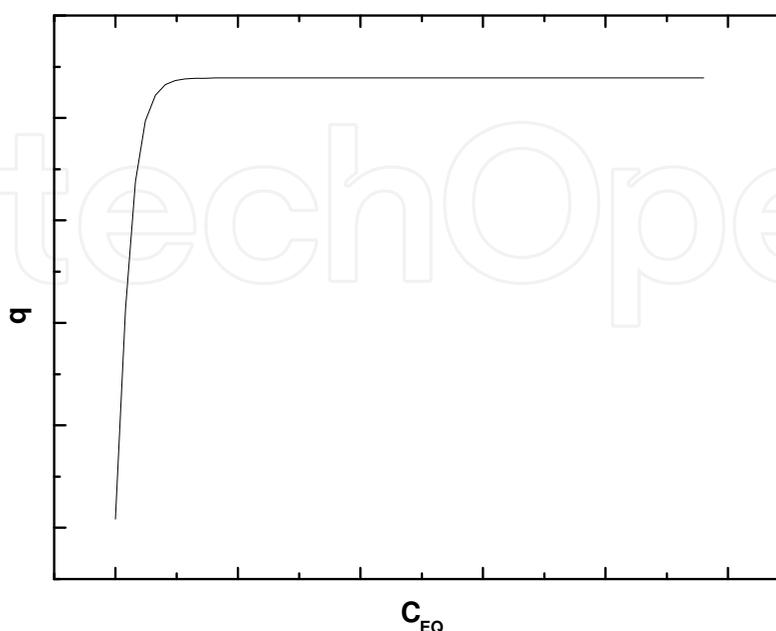


Fig. 1. Typical curve of an adsorption isotherm. Source: Oliveira, 2011.

These isotherms generally are associated mainly to Langmuir and Freundlich besides other models derived of these firsts. The Freundlich model suggests adsorbed monolayers, where the interactions among adjacent molecules that are adsorbed: the energy distribution is heterogeneous due to the diversity of the binding sites and the nature of the adsorbed metallic ions. The Langmuir model considers an adsorbed monolayer with homogeneous distribution of binding sites and adsorption energy, without interaction among the adsorbed molecules (Selatnia et al., 2004).

For instance, on biosorption of Sm(III) and Pr(III) by *Sargassum* sp. biomass described by Oliveira et al. (2011), the Langmuir adsorption model has been founded very accurate, that is approximated for liquid-solid equilibrium by the Eq. (2) and it can be observed in the Fig. 2.

$$q = (q_{\text{MAX}}bC_{\text{EQ}})/(1+bC_{\text{EQ}}) \quad (2)$$

where q is the metal uptake; q_{MAX} is the maximum biosorption uptake that is reached when biomass active sites are saturated by the metals; b is a constant that can be related to the affinity between the metal and the biomass; and C_{EQ} is the metal concentration in the liquid phase after achieving the equilibrium.

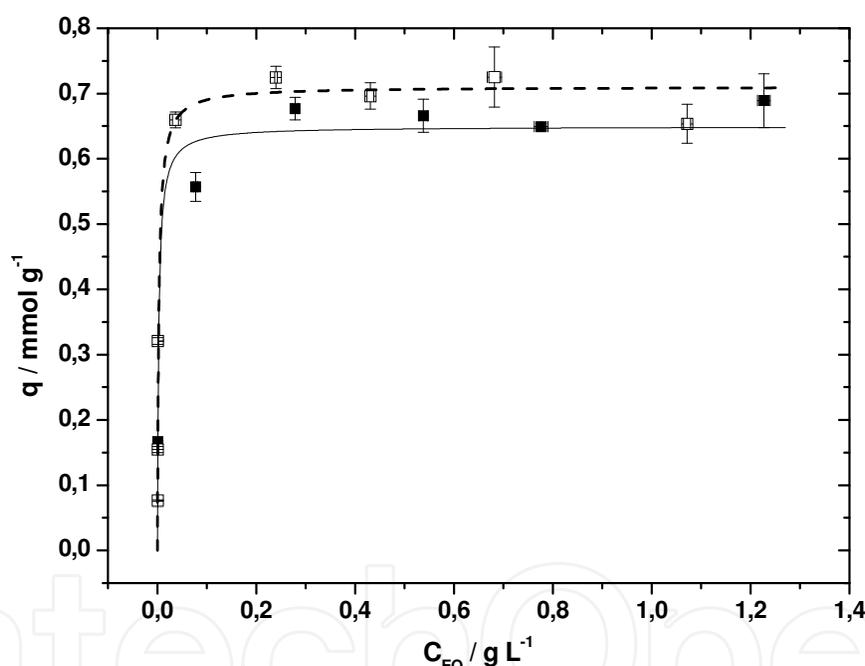


Fig. 2. Biosorption isotherms for Sm(III) and Pr(III) solutions by *Sargassum* sp. described by the Langmuir adsorption model. Symbols: (—■—) Sm(III) and (—□—) Pr(III).

Source: Oliveira et al., 2011.

Additionally, it is noteworthy that the shape of the biosorption isotherms (Fig. 2) approaches the profile of irreversible isotherms: the initial slope is very steep and the equilibrium plateau is reached at low residual concentration. This can be correlated to the great affinity of Sm(III) and Pr(III) for the biosorbent (Oliveira et al., 2011).

The models presented on Table 4 are applied for mono-component systems. For systems with more than one metallic species, the mathematical modeling must be modified to take into account the competition of metal by the binding sites (Aksu & Açıkel, 2000). Some approaches are listed on Table 5.

Adsorption Model	Equation	Advantages	Disadvantages
Langmuir	$q_i = (q_{MAX,i} b_i C_{EQ,i}) / (1 + \sum_{i=1}^n b_i C_{EQ,i})$	Constants have physical meaning; Isotherms levels off at maximum saturation	Not structured; Does not reflect the mechanism well
Combination Langmuir-Freundlich	$q_i = (a_i C_{EQ,i}^{1/n_i}) / (1 + \sum_{i=1}^n b_i C_{EQ,i}^{1/n_i})$	Combination of above	Unnecessarily complicated
Surface complexation model	$q \sim f(C_{EQ})$, could follow e.g. Langmuir	Model more structured: intrinsic equilibrium constant could be used	Equilibrium constants have to be established for different types of binding

Table 5. Examples of physicochemical multi-component models of adsorption. Source: Volesky, 2003.

5.2 Biosorption kinetics

Biosorption processes tend to occur rapidly, taking from few minutes to a couple of hours and it takes account transfer mass processes and adsorption processes. The biosorption kinetics is controlled mainly by convective and diffusive processes. In a first stage occurs the metal transference from solution to adsorbent surface neighborhood; then in the next step, the metal transference from adsorbent surface to intraparticle active sites; and finally, the metallic ion removal by the active sites via complexation, adsorption, or intraparticle precipitation. The first and second steps represent the resistance to convective and diffusive mass transferences and the last one is quick and non-limiting for the overall biosorption velocity (Selatnia et al., 2004).

Analogously to the biosorption isotherms, the biosorption kinetics in general present hyperbolic shape (as the Fig. 1) and they are described by various models. The models more used in biosorption studies are presented on Table 6.

Adsorption model	Differential equation	Integral equation	Initial adsorption velocity
Pseudo-first-order	$dq_t/dt = k_1(q_{EQ} - q_t)$	$\ln(q_{EQ} - q_t) = \ln q_{EQ} - k_1 t$	$v_1 = k_1 q_{EQ}$
Pseudo-second-order	$dq_t/dt = k_2(q_{EQ} - q_t)^2$	$q_t = t / [1 / (k_2 q_{EQ}^2) + t / q_{EQ}]$	$v_2 = k_2 q_{EQ}^2$

Table 6. Examples of kinetics models used in biosorption studies. Source: Wang & Chen, 2009.

The pseudo-second-order model is preferred for biosorption of RE (Oliveira & Garcia Jr., 2009; Oliveira et al., 2011) and is represented by the integral Eq. (3).

$$q_t = t / [1 / (k_2 q_{EQ}^2) + t / q_{EQ}] \quad (3)$$

where q_t is the biosorption uptake in the t time of assay; q_{EQ} is the equilibrium metal uptake; and k_2 is a constant that represent the metal access rate to biomass in the pseudo-second-order kinetic model. Fig. 3 displays the modeling of samarium and praseodymium biosorption kinetics in *Sargassum* sp. by the pseudo-second-order kinetics model.

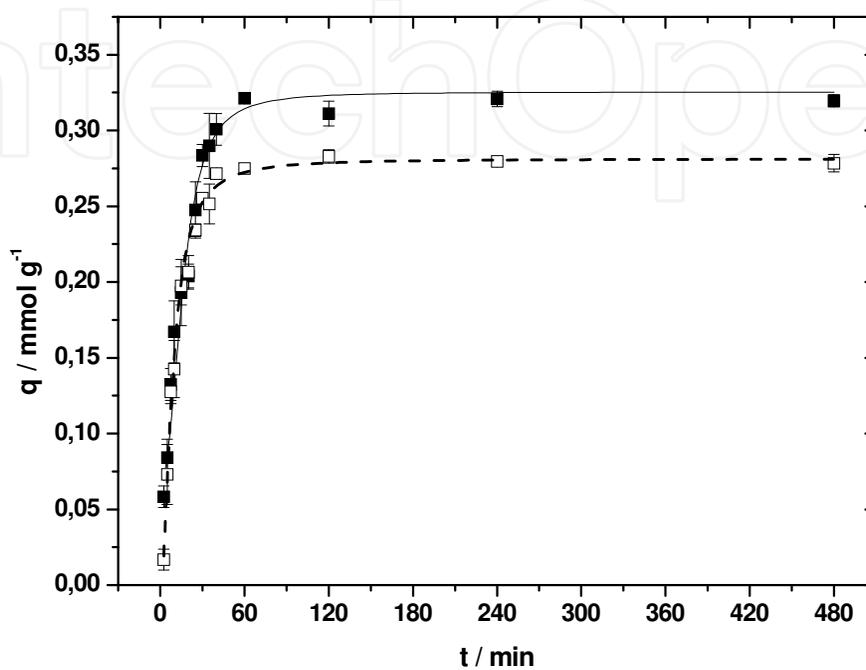


Fig. 3. Biosorption kinetics for Sm(III) and Pr(III) solutions by *Sargassum* sp. described by the pseudo-second-order kinetics model. Symbols: (—■—) Sm(III) and (---□---) Pr(III). Source: Oliveira et al., 2011.

5.3 Chemical speciation and pH

Generally the biosorption carried out in low pH values (smaller than 2.0) has a non-effective metal uptake (for the cases that metallic cationic species are involved) because the high hydronium concentration makes the competition among these protons more favorable than the metals in solution by the biomass active sites. Moreover the acidic groups in low pH should be protonated according with their pKa values as can be seen on Table 1.

The metal uptake is increased when the acidic groups tend to be deprotonated from their pKa values (Table 1) and the metallic ion presents a chemical speciation that provides greater adsorption performance. In the case of RE biosorption for *Sargassum* sp. biomass, Palmieri et al. (2002) and Diniz & Volesky (2005) founded that the biosorption of La(III), Eu(III), and Yb(III) is more effective in crescent pH values (2.00 to 5.00) because the quantity of negative ligands is increased, and consequently the increase of the attraction among the ligands and the metallic cations. The optimal pH for *Sargassum* founded about 5.0. In this pH the carboxyl pK_as of mannuronic and guluronic acid residues (3.38 and 3.65, respectively) in the alginate biopolymer (main component of brown algae cellular envelope) are suppressed; so all carboxyl sites should be more available for the adsorption. Towards the RE speciation in distinct pH ranges: (a) in pH < 6.0 prevail the presence of RE³⁺; (b) between about 6.0 < pH < 9.5 there is the generation of RE(OH)²⁺ and RE(OH)²⁺ that remain

solubilized or suspended in solution; and (c) from pH \sim 8.5 occurs the precipitation of RE hydroxide. Biosorption of anionic species are very less common and occurs when a metallic complex is formed with a negative global charge, e.g. the AMT-BIOCLAIM™ is able to adsorb gold, zinc, and cadmium from cyanide solution (i.e. cyanide complexes with the metals) in metal-finishing operations (Atkinson et al., 1998).

5.4 Temperature

In general, the literature describes that the biosorption process is not influenced between 20 and 35°C (Vegliò & Beolchini, 1997). However some biosorbent present considerable differences on biosorption performance as function of the temperature. For instance, Ruiz-Manríquez et al. (1998) studied the biosorption of copper on *Thiobacillus ferrooxidans* [sic] considering temperatures of 25 and 37 °C: the results indicate that there was a positive effect in the biosorption uptake when the temperature was increased, where the increase in the biosorption was of 68%.

Besides the evaluation of the optimal temperature to be used in biosorption purposes, the batch procedures commonly can be utilized to find thermodynamic parameters as enthalpy (ΔH), entropy (ΔS), and Gibbs free-energy (ΔG) through the Eqs. (4) and (5).

$$\Delta G = -RT \ln K_{EQ} \quad (4)$$

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

where R is the gas constant (8.314 J/(K mol)), T is the temperature, and K_{EQ} is equilibrium constant in determined temperature that corresponds the ratio between the equilibrium metal concentration in the liquid (C_{EQ}) and solid phases (q_{EQ}). In this context, Dos Santos et al. (2011) verified that the chemical modification of the sugarcane bagasse by different treatments lead a more energetically favorable adsorption of copper in comparison with raw material, because the negative increase of the Gibbs free-energy.

5.5 Presence of counter-ions

The binding of metallic ions biomasses is influenced by other ionic species, such as cations and anions present in solution. Benaissa & Benguella (2004) describe the influence of the presence of cations (Na^+ , Mg^+ , and Ca^{2+}) and anions (Cl^- , SO_4^{2-} , and CO_3^{2-}) on cadmium biosorption for chitin. The presence of these ions in solution inhibits the uptake of cadmium by chitin to different degrees: sodium and chloride ions have no significant. For magnesium, calcium, sulfate, and carbonate ions the effects ranged from a large inhibition of cadmium by calcium and carbonate to a weak inhibition by magnesium and sulfate. These interferences in cadmium biosorption are resulted of the competition among the interesting metal and the counter-ion by the binding sites.

Additionally, Palmieri et al. (2002) studied the lanthanum biosorption by *Sargassum fluitans* in solution with chloride and sulfate ions: at same pH it was observed higher maximum metal uptake values for the biosorption on presence of chloride, as such can be seen on Fig. 4. In the case of lanthanides, the formation of complexes with chloride or sulfate affects the coordination sphere of metal, leading to an influence on the net charge of the cation. Chloride ions are reported to have an outer sphere character with a less disturbance in the hydration sphere. On the other hand, sulfate and carboxylate anions present inner sphere character more pronounced in the complex formation with lanthanum. The biosorption

uptake of lanthanum presents higher value for chloride-based solutions than sulfate-based solutions could suggest that the fewer disturbances on the inner coordination sphere caused by chloride anion facilitate the interaction with carboxylate groups present in the biomass.

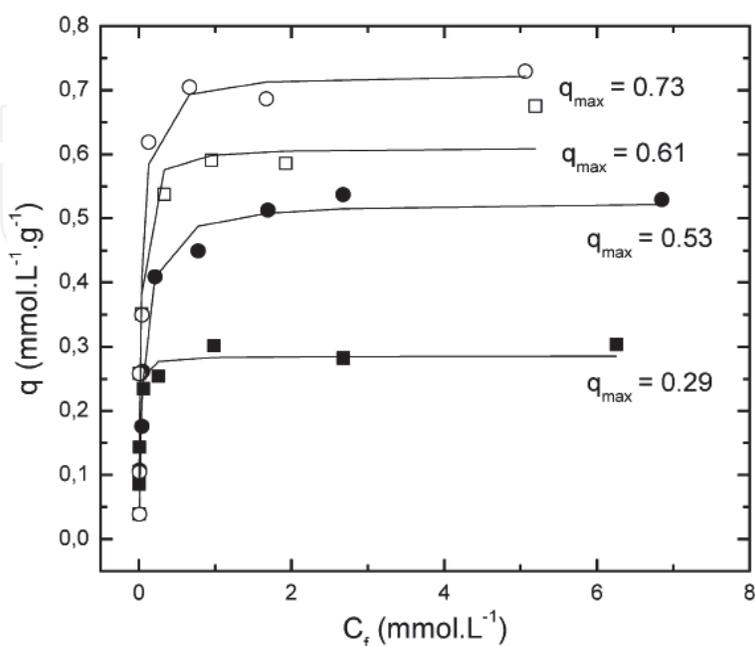


Fig. 4. Bisorption isotherms for La(III) on *Sargassum fluitans* from chloride or sulfate-based solutions at different pHs. Symbols: chloride-based solutions at (\square) pH 4 and (\circ) pH 5; and sulfate-based solutions at (\blacksquare) pH 4 and (\bullet) pH 5. Source: Palmieri et al., 2002.

5.6 Desorption

After the metal removal from aqueous solutions by the biomass, it is important the metal recuperation from biomass. In this point, it is achieved the metal desorption process, whose aim is the weakening the metal-biomass linkage (Modak & Natarajan, 1995). Generally it can be applied diluted mineral acids and complexing agents as desorbents. Biosorption and desorption isotherms present close behavior characteristic of Langmuir modeling, which has at equilibrium equivalent kinetic rates (Palmieri et al., 2002).

Diniz & Volesky (2005) evaluate the reversibility of the adsorption reaction for the biosorption of lanthanum, europium, and ytterbium by *Sargassum polycystum* using the desorbent agents: nitric and hydrochloric acids, calcium nitrate and chloride salts, EDTA, oxalic and diglycolic acids. This work as such other studies founded the hydrochloric acid as the best agent for brown algae, with percentage of recovery between 95-100%.

5.7 Biomass characterization from analytic and spectroscopic methodologies

Beyond the perspectives of application of the biosorption in order to optimize the process, the understanding of the mechanisms involved in the biosorption is justifiable for better comprehension of the process and of itself scale-up. This is carried out from qualitative and/or quantitative characterizations by potentiometric titrations, and spectroscopic and microscopic techniques as such FTIR (Fourier transform infrared spectroscopy), SEM (scanning electron microscope), EDX (energy-dispersive X-ray spectroscopy), XPS (X-ray photoelectron spectroscopy), etc. The main objective of the biosorbent characterization has

been to identify the chemical groups involved in the biosorption and the way that these groups perform the metal binding.

The most common technique used is the potentiometric titration, which evaluate the existence of stoichiometric relationships among the metals and the binding sites, and to determine the pK_a s values of the chemical groups on biomass cellular envelope. The Table 1 summarizes the characteristics of the protonated *Sargassum* sp. biomass before and after samarium and praseodymium biosorption.

Material	Strong acid groups (mmol/g)	Total amount of acid groups (mmol/g)	Weak acid groups (mmol/g)	Occupancy of binding sites (%)
Protonated biomass	0.15	1.77	1.62	-
Sm(III) - loaded biomass	0.07	1.26	1.19	29
Pr(III) - loaded biomass	0.07	1.18	1.11	33

Table 7. Acid-base properties of protonated *Sargassum* sp. before and after Sm(III) and Pr(III) biosorption. Source: Oliveira et al., 2011.

The strong acid groups counted for only 0.15 mmol/g on protonated biomass, and decreased to 0.07 mmol/g after the biosorption of either Sm(III) or Pr(III). These groups of lowest pK_a have been identified as the ester sulfate groups of the fucoidan, which are present on the cell wall of brown seaweeds. Weak acid groups are mainly constituted by carboxylate groups from alginate compounds, which represent more than 90 % of total acid groups, i.e., 1.62 mmol/g. After metal biosorption the titration identified 1.19 and 1.11 mmol/g of weak acid groups for Sm(III) and Pr(III), respectively. Thereby only around 30 % of the acid groups were involved in metal binding (Oliveira et al., 2011).

Another example of the biomass characterization can be observed on Fig. 5, which displays the analysis of SEM-EDX of *Sargassum* sp. biomass after lanthanum biosorption. The lanthanum presence in the X-ray spectra confirms the adsorption of the metal on the biosorbent surface. In the SEM micrography also is evident the surface colonization by diatoms as well as the assignments of chemical elements from the marine environment (calcium, aluminum, silicon).

6. Biosorption in fixed-bed columns

Despite of the biosorption in batch systems to available parameters to understand the metal-biomass interaction and to select the best operational condition, the procedures in columns are generally the preferential mode for the biosorption application in the industrial scale-up, once that the process can be performed continuously (Vieira et al., 2008; Volesky, 2003). This operational mode is more appropriate for large-scale applications in industry than other types of reactors as such agitated tanks, fluidized-bed columns, etc. The fixed-bed columns have a series of advantages: they have simple operation, they achieve large yields, and they have ease scale-up from procedures in laboratorial scale (Borba et al., 2006; Borba et al., 2008; Valdman et al., 2001; Vijayaraghavan et al., 2005; Vijayaraghavan & Prabu, 2006). The use of fixed-bed columns allow to avoid separation difficulties between the biosorbent and the effluent (Kentish & Stevens, 2001). This experimental procedure has as limiting step the mass transfer of metal from solution to the biosorbent, since the adsorption reactions do not limit the process due to the fast kinetics (Aksu, 2001; Crini, 2005; Volesky, 2001).

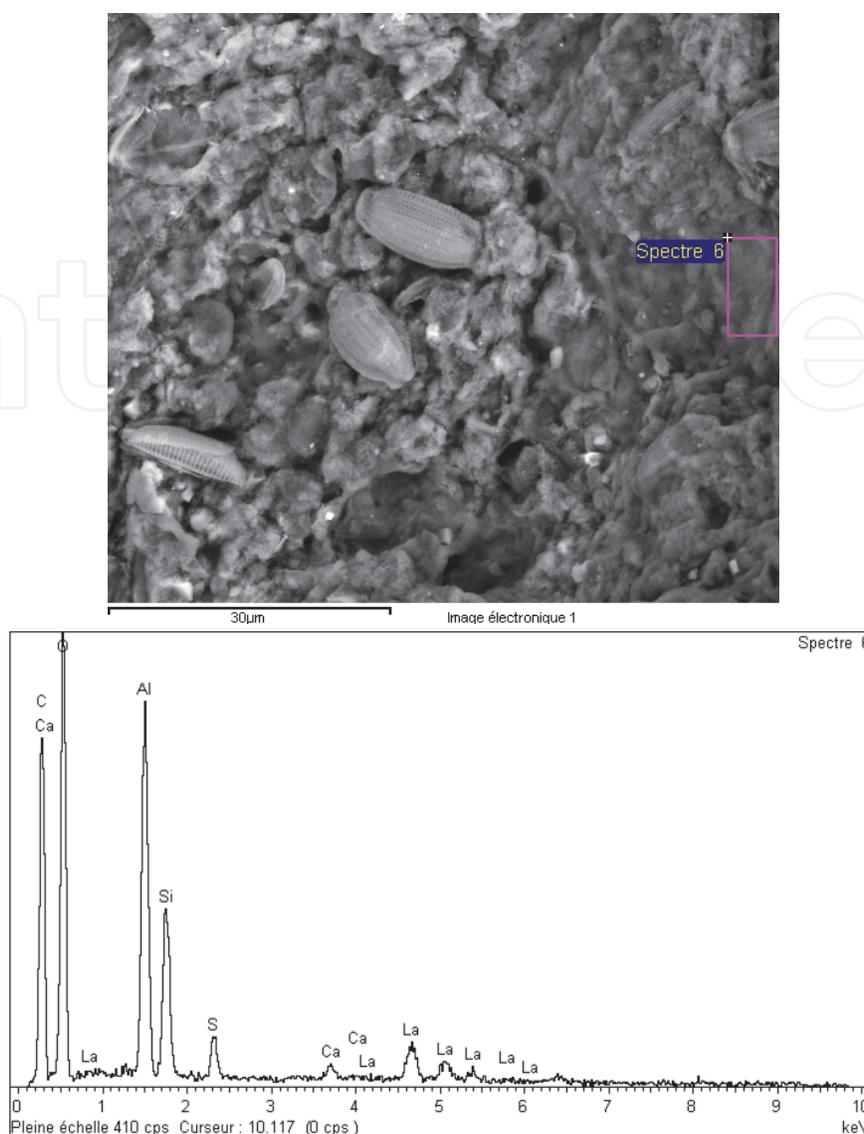


Fig. 5. Scanning electronic micrography of *Sargassum* sp. biomass after lanthanum biosorption and related X-ray spectra. Source: Oliveira, 2011.

6.1 Biosorption: frontal analysis and breakthrough curves

The main methodologies for the concentration, separation, and purification of metals involve a great number of equilibriums and phase transferences, such as the methodologies listed in Table 8.

Methodology	Concentration applied (g/L)
Solvent extraction	0.5-500
Microporous membranes	10 ⁻² -10
Emulsified or supported liquid membranes	10 ⁻⁴ -10
Ion-exchange	10 ⁻⁶ - 1
Biosorption	10 ⁻⁶ - 0.1

Table 8. Separation technologies and concentration ranges applied. Source: Kentish & Stevens, 2001.

The biosorbents should have several mechanisms of metal uptake, but for column biosorption perspectives these mechanisms are approximated to mainly ion-exchange or adsorption. Generally the chromatographic separations by fixed-bed columns occur by two ways: the frontal analysis and the displacement elution.

On frontal analysis is carried out the metal adsorption for a percolated volume of solution in the column, which produces a mixed zone of metallic ions that spreads to a distance across the column according to the individual and competitive interactions among the metals and the adsorbent. In this process, the mixed zone is composed by several equilibriums among the displaced ions and the retained ions and it moves across the column without to alter your volume. After the mixed zone is displaced to sufficient distance across the column, it is reached an equilibrium which the components are resolved in differentiate heights, i.e. in distinct or enriched zones for each one of the components (Fritz, 2004). Thus the greater interaction among the metals and the biosorbent represents a greater retention of these metals across the column. Therefore, a greater number of distinct affinities of the percolated metals by the adsorbent mean a better possibility of the system to resolve the metals in differentiate heights.

Commonly the frontal analysis performance is mathematically quantified and modeled from the application of approximations and boundary conditions on non-linear material balance equations based mainly for biosorption columns on equilibrium dispersive model (Guiochon et al., 2006). The model assumes that all conditions are due to a non-equilibrium, which is treated into a term of apparent axial dispersion, where it is considered that the dispersion coefficients of the components remain constants. The column is considered unidimensional and radially homogenous, i.e. the properties are constants in a same cross section. When a fixed-bed column is occupied by fluid with a constant linear velocity, the differential mass balance involved is given by the Eq. (6).

$$\partial q(t,z)/\partial t + v[\partial C(t,z)]/\partial z + [(1-\epsilon)/\epsilon][\partial q(t,z)/\partial t] - D_L[\partial^2 C(t,z)]/\partial z^2 = 0 \quad (6)$$

where t is the time; z is the axial coordinate with origin on column entrance; q is the metal uptake in the stationary phase; C is the concentration in the mobile phase; v is the linear velocity; $(1-\epsilon)/\epsilon$ is the phase ratio (mobile phase volume/stationary phase volume) and ϵ is the adsorbent porosity; and D_L is a parameter that includes the contributions of the axial dispersion (due to molecular diffusion), the non-homogeneity of the flux (eddy diffusion), and the bed tortuosity.

The terms on Eq. (6) represent respectively: (a) the accumulation in the stationary phase; (b) the convective phenomena; (c) the accumulation in the mobile phase, and (d) the diffusive phenomena. Some approximations should be achieved as such: (a) the column should be considered radially homogenous only in isothermic or isobaric operations; (b) the compressibility of the mobile phase is neglected between 0 and 200 bar in the mostly cases if the volume is altered between 0.5 and 2%; (c) the viscosity in the mobile phase is constant; (d) since the pump provides constant flow rate, the velocity is also constant; (e) the parameter D_L is constant; (f) the partial molar volume of the sample components is constant in both phases; (g) the solvent is not adsorbed; (h) constant operational conditions: temperature, pressure, flow rate, physicochemical parameters, porosities, etc. (Guiochon et al., 2006).

There are several parameters that govern the adsorption, which may be modified to find a more effective adsorption and/or a separation with better resolution of the components as

such: (a) the column geometry that considers the height and the cross section area of the bed; (b) the homogeneity or the heterogeneity of the adsorbent; (c) the particle diameter and their implications on porosity, packing, and tortuosity of the bed; (d) the number of theoretical plates; (e) the concentration and composition of the solute on mobile and stationary phases; (f) the presence of additives on feeding, e.g. complexing agents, buffers, etc.; (g) the column flow rate; etc. (Guiochon et al., 2006).

In biosorption isotherms, the concentration profiles in the liquid and solid phases change in space and time. Thereby the development and performance of adsorption columns are difficult to reach without an approximated quantitative modeling of the Eq. (6). From perspective of design and optimization of the column processes, the behavior in fixed-bed is described by the effluent concentration profile (C/C_0 , where C and C_0 are the concentration of eluate and eluent, respectively) in function of the time or percolated volume (Nadaffi et al., 2007), i.e. by breakthrough curve, which is showed on Fig. 6. The curve shape is given by a sigmoid function and it is determined by the shape of the equilibrium isotherm, i.e. it is influenced by the transport processes and the adsorbent nature (Chu, 2004).

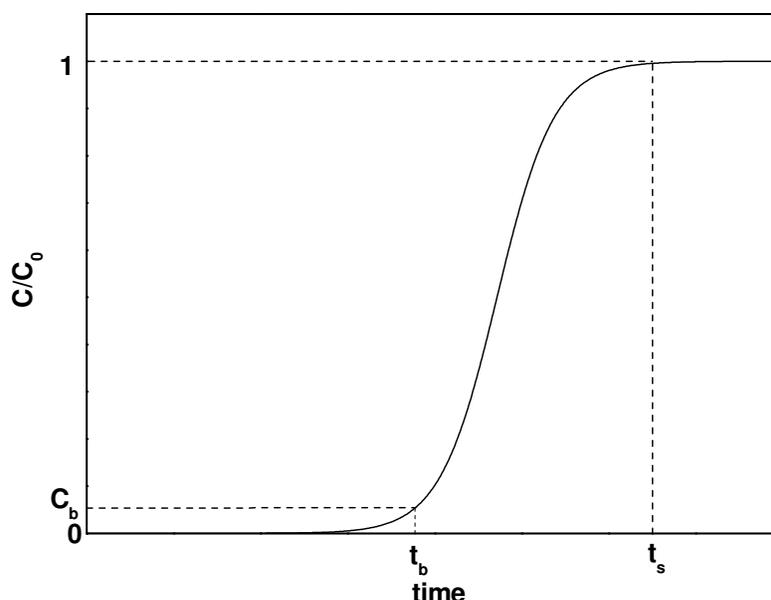


Fig. 6. Schematic representation of the breakthrough curve. Source: Oliveira, 2011.

In the breakthrough curves (Fig. 6) are determined the breakthrough and saturation times (t_b and t_s , respectively). The breakthrough time indicates the instant in which the metallic ion is effectively discharged on eluate, and the saturation time corresponds to the instant of metal mass saturation on biomass. The breakthrough time is arbitrarily inferred for C/C_0 at 0.05; while the saturation time is defined ideally when C/C_0 values reach 1.0 (generally at 0.90-0.95). All optimized system in columns is based on accurate prediction of the breakthrough time under selected operational conditions. When the eluate concentration reaches a predefined level, the column operation is finalized; in this point the regeneration process may be achieved to activate the column for a next operation cycle (Kentish & Stevens, 2001). In order to investigate the alternatives for the separation of metallic species, the breakthrough time is crucial because it represents the interaction between the metal and the biomass; so if the breakthrough time is great, this indicates that the interaction between the metal and the biomass is greater.

The variation between the breakthrough and saturation times depends on the capacity of the column toward the quantity of applied metal (Aksu, 2001). A more efficient adsorption performance will be obtained as greater is the curve slope, i.e. as smaller is the gap between the breakthrough and saturation times (Fig. 6) (Chu, 2004). This gap corresponds to the extension of the mass transfer zone (MTZ) on bed (Nadaffi et al., 2007), which is the bed active region where the adsorption occurs as can be seen on Fig. 7. So the column efficiency will be better in smaller values of height of mass transfer zone which indicate a behavior near to ideality; in that case a step function where the curve inclination between the breakthrough and the saturation tends to zero.

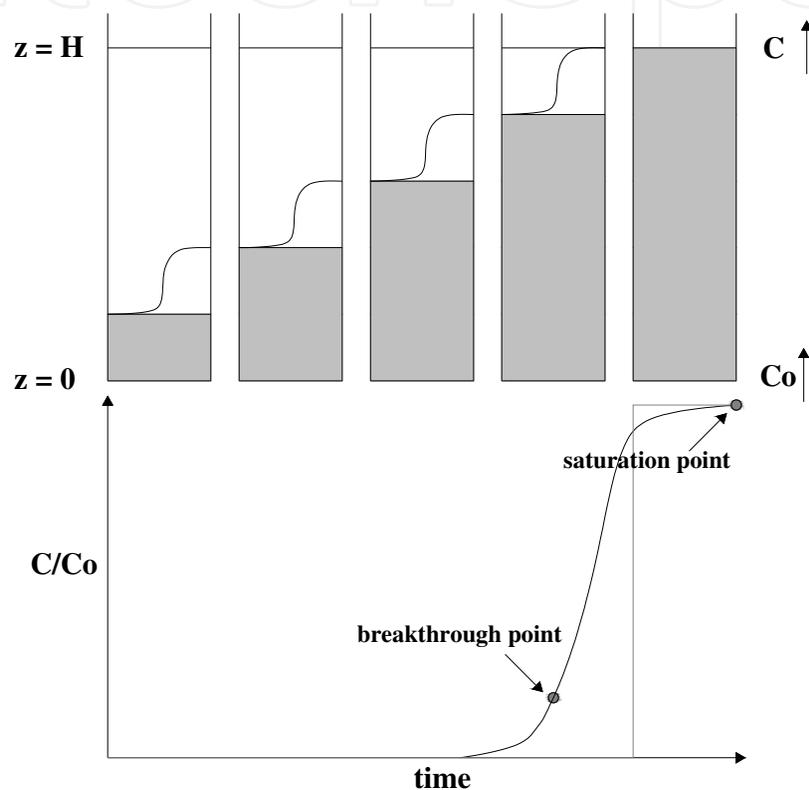


Fig. 7. Schematic representation of the movement of the mass transfer zone in fixed-bed column. Symbols: (—) ideal and (---) real cases. Source: Oliveira, 2011.

Several derivations may be used from the material balance in the Eq. (6) to perform the breakthrough curves such as the models of Thomas, Bohart-Adams, Yoon-Nelson, etc. Some models are described in function of operational and kinetic parameters (e.g. Thomas and Bohart-Adams); in other hand, there are models related to adjustment purely mathematic according with the sigmoid function (e.g. Yoon-Nelson model). For instance the Thomas model is expressed Eq. (7).

$$C/C_0 = 1/\{1+\exp[(k_{Th}/Q)(q_{MAX}M-C_0V)]\} \quad (7)$$

where k_{Th} is the Thomas constant; Q is the flow rate; q_{MAX} is maximum biosorption uptake; M is the dry mass of biomass; and V is the volume percolated. The Fig. 8 presents the experimental data for column biosorption of lanthanum by *Sargassum* sp. adjusted by the Thomas model.

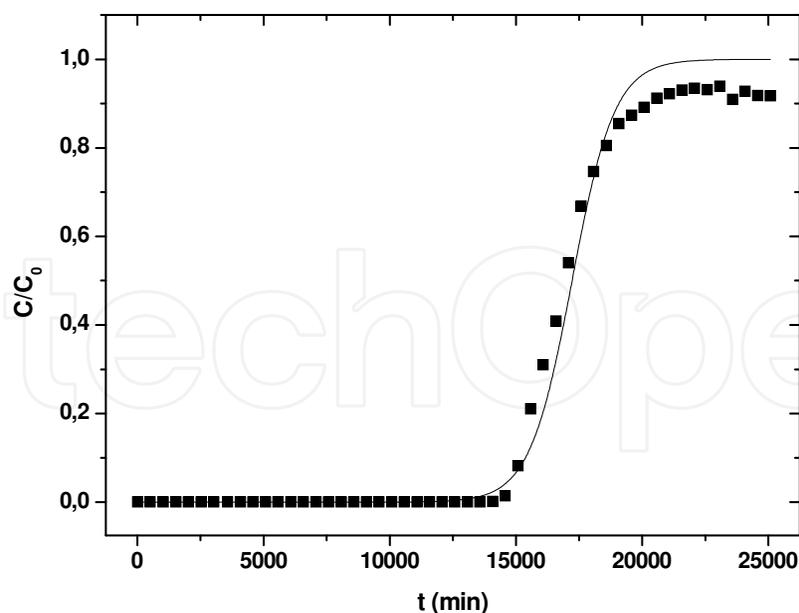


Fig. 8. Modeling of breakthrough curve in the column biosorption of La(III) for *Sargassum* sp. biomass by the Thomas model. Symbols: (■) data of metal concentration on eluate and (---) curve fit for Thomas model. Source: Oliveira, 2011.

6.2 Dependence of the operational parameters

There is broad literature that describes the effects of operational parameters to augment and to improve the biosorption in fixed-bed columns (Chu, 2004; Hashim & Chu, 2004; Kratochvil & Volesky, 2000; Naddafi et al., 2007; Oliveira, 2007; Oliveira, 2001; Valdman et al., 2001; Vieira et al., 2008; Vijayaraghavan et al., 2005; Vijayaraghavan et al., 2008; Vijayaraghavan & Prabu, 2006; Volesky et al., 2003). These parameters modified mainly related are: flow rate, feeding concentration, height of packed-bed column, porosity, mass of biomass, etc. Vijayaraghavan & Prabu (2006) evaluate some variables as the bed height (15 to 25 cm), flow rate (5 to 20 mL/min), and copper concentration (50 to 100 mg/L) in *Sargassum wightii* biomass from breakthrough curves: each variable evaluated was changed and the others were fixed. Continuous experiments revealed that the increasing of the bed height and inlet solute concentration resulted in better column performance, while the lowest flow rate favored the biosorption (Vijayaraghavan & Prabu, 2006)

Naddafi et al. (2007) studied the biosorption of binary solution of lead and cadmium in *Sargassum glaucescens* biomass from the breakthrough curves modeled according with the Thomas model (eq. (7)). Under selected flow rate condition (1.5 L/h) the experiments reached a selective biosorption. The elution of the metals in distinct breakthrough times with biosorption uptake in these times at 0.97 and 0.15 mmol/g for lead and cadmium, respectively.

6.3 Desorption: chromatographic elution and biomass reuse

Column desorption is used for the metal recovery, but this procedure under selected conditions may be operated to carry out chromatographic elution by the displacement of the adsorbed components in enriched fractions containing each metal (Diniz & Volesky, 2006). This is resulted of the simple drag of the previous separation on frontal analysis. Nevertheless the eluent may present differential affinity by the adsorbed solutes, so there is

the possibility to use the procedure to promote a more effective separation of the components. The chromatographic elution is dependent of the parameters referred to frontal analysis and of the composition and concentration of the displacement solution. Desorption profiles are given as bands or peaks whose modeling are associated directly to mathematic approximations by Gaussian functions that may be modified or not exponentially (Guiochon et al., 2006).

A typical column desorption with hydrochloric acid from *Sargassum* sp. previously submitted to biosorption of lanthanum is showed on Fig. 9, which is represented by lanthanum concentration in eluate as function of the volume.

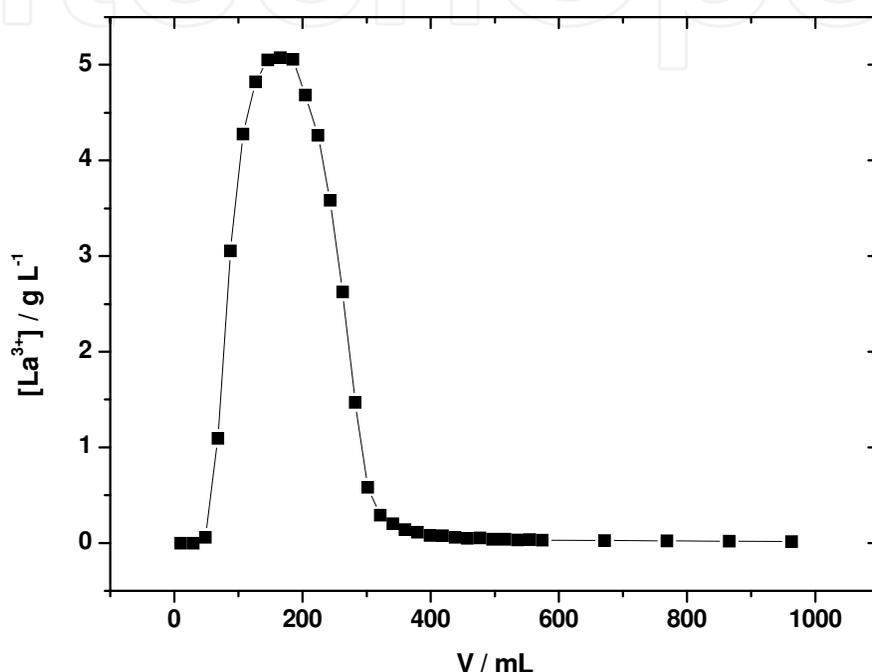


Fig. 9. Column desorption of La(III) from *Sargassum* sp. biomass with HCl 0.10 mol/L. Symbols: (-■-) metal concentration on eluate. Source: Oliveira, 2011.

On Fig. 9 can be seen that after the start of the acid percolation occurs a quick increase of concentration until the maximum to 5.08 g/L for lanthanum. Parameters as the recovery percentage (p) and concentration factor (f) are obtained from biosorption and desorption curves. The recovery percentage is resulted of the ratio between the values of metal recovery on desorption and maximum metal uptake on biosorption, while the concentration factor refers to the ratio between the saturation volume on biosorption and the effective recovery volume on desorption. Both measure the efficiency of the desorbing agents in the metal recovery. For instance, these parameters obtained from Fig. 9 were 93.3% and 60.4 times of recovery percentage and concentration factor, respectively; which are expressive and satisfactory for the column biosorption purposes (Oliveira, 2011).

For biosorption and desorption processes, other important aspect is the biosorbent reuse for recycles biosorption-desorption according the cost benefit between the biosorption capacity loss during desorption steps and the metal recuperation operational yield (Diniz & Volesky, 2006; Gadd, 2009; Godlewska-Zylkiewicz, 2006; Gupta & Rastogi, 2008; Volesky et al., 2003). Oliveira (2007) performed the neodymium column biosorption by *Sargassum* sp. and the subsequent desorption in three recycles. In these experiments was observed that occurs a

decrease in mass metal accumulation through the cycles. Accumulation decrease from first to third cycle in 22%, which is due to the partial destruction of binding sites on desorption procedures, and the binding sites blocking by neodymium ions strongly adsorbed. The result showed that the biomass may be used for recycle finalities.

The loss in performance of the adsorption during the recycles can have numerous origins. Generally they are associated to the modifications on chemistry and structure of the biosorbent (Gupta & Rastogi, 2008), and the changes of access conditions of the desorbent to the metal and mass transfer. Low-grade contaminants in the solutions used in these procedures may accumulate and to block the binding sites or to affect the stability of these molecules (Volesky et al., 2003).

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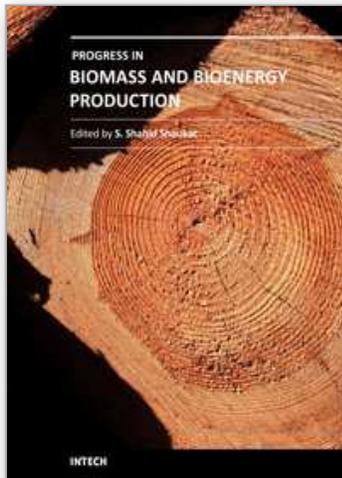
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Progress in Biomass and Bioenergy Production

Edited by Dr. Shahid Shaukat

ISBN 978-953-307-491-7

Hard cover, 444 pages

Publisher InTech

Published online 27, July, 2011

Published in print edition July, 2011

Alternative energy sources have become a hot topic in recent years. The supply of fossil fuel, which provides about 95 percent of total energy demand today, will eventually run out in a few decades. By contrast, biomass and biofuel have the potential to become one of the major global primary energy source along with other alternate energy sources in the years to come. A wide variety of biomass conversion options with different performance characteristics exists. The goal of this book is to provide the readers with current state of art about biomass and bioenergy production and some other environmental technologies such as Wastewater treatment, Biosorption and Bio-economics. Organized around providing recent methodology, current state of modelling and techniques of parameter estimation in gasification process are presented at length. As such, this volume can be used by undergraduate and graduate students as a reference book and by the researchers and environmental engineers for reviewing the current state of knowledge on biomass and bioenergy production, biosorption and wastewater treatment.

How to reference

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Robson Oliveira, Mauricio Palmieri and Oswaldo Garcia Jr. (2011). Biosorption of Metals: State of the Art, General Features, and Potential Applications for Environmental and Technological Processes, Progress in Biomass and Bioenergy Production, Dr. Shahid Shaukat (Ed.), ISBN: 978-953-307-491-7, InTech, Available from: <http://www.intechopen.com/books/progress-in-biomass-and-bioenergy-production/biosorption-of-metals-state-of-the-art-general-features-and-potential-applications-for-environmental>

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