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The fundamental proton binding properties of biosorbents

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Abstract

A broad variety of materials of biological origin have been successfully used in recent decades for the removal of pollutants from solution. These biosorbents present a range of natural polymers that play a key role on their adsorption capacity. It is therefore critical to understand the physicochemical properties of the chemical groups that form these polymers. The acid-base properties of biomass are affected by pH, ionic strength and medium composition. Nevertheless, these crucial parameters are not always considered during biosorption studies.

According to bibliography, less than 3% of biosorption papers include studies on proton binding. Moreover, in 60% of these papers there is key experimental information missing such as the calibration of the electrodes employed in potentiometric titrations. We consider therefore that there is an important need for reviewing the role of proton binding on biosorption studies. This paper outlines the major advances on proton binding data interpretation and modelling on biosorbents. In addition, we propose some experimental considerations that cover all issues raised in this paper concerning the acid-base properties of biosorbents.

Keywords: Biosorption, proton binding, master curve, electrostatics and non-electrostatic effects, Hofmeister series.

1. Introduction

The removal of pollutants (e.g. heavy metals, phenols, dyes, endocrine disruptors, etc.) from contaminated waters is an issue of current concern. For example, in 2015 the percentage of untreated wastewaters in high- and low-income countries was c.a. 30 and 92%, respectively (Koncagül et al. 2017).

The search for an efficient, affordable and easy-to-handle technology has produced a potential alternative to traditional wastewater treatments such as ionic exchange or precipitation; that is the use of green adsorbents. These materials of biological origin are usually referred to as biosorbents, and the technique involving their use for pollutant removal from waters, biosorption (Volesky 2003).

A broad variety of materials have been used in biosorption studies in recent decades (De Gisi et al. 2016): e.g. algae (Davis et al. 2003), bacteria (Gupta and Diwan 2017; Vijayaraghavan and Yun 2008), fungi (Kapoor and Viraraghavan 1995), agricultural by-products (Bhatnagar and Sillanpää 2010) or chitin and wood derivatives (Abdolali et al. 2014; Gerente et al. 2007). The biosorbents present a heterogeneous matrix that constitutes the biomass structure, and is formed of polysaccharides (Crini 2005). The excellent pollutant adsorption capacity reported for many biosorbents results from the presence of specific chemical groups in their biopolymer chains. It is therefore critical to understand the physicochemical properties of these natural polymers present in the biomass used in biosorption studies.

The biosorption mechanism is complex due to the heterogeneity and structure of the biosorbents (Aksu 2005; Robalds et al. 2016). Different chemical active functional groups, such as carboxyl, hydroxyl, sulfonate, acetamide or amino groups are present in the polysaccharides that form the structure of biosorbents (Volesky 2003). Those chemical groups are responsible for pollutant removal. Specifically, the removal of contaminants from solution depends on the affinity between the binding sites and the pollutants (namely, the specific equilibrium constants), the availability of the binding sites, i.e. chemical state of the groups, their quantity and accessibility (Schiewer and Volesky 2000). Therefore, the biosorption mechanism is also influenced by factors such as the pH, temperature and solution composition, or the concentration and type of contaminant.

Protons and covalently bound contaminants (e.g. heavy metals) compete for the same binding sites. This competition, together with pollutant speciation, makes the solution pH a key parameter in biosorption studies. In addition, the binding of contaminants to biosorbents can be largely influenced by charge behaviour, also regulated by the solution pH (de Wit et al. 1993). When biosorbents are fully protonated many chemical groups (carboxyl, hydroxyl, sulfonate, etc.) present no charge, while those groups are negatively charged when deprotonated. At pH values higher than the pK of the binding groups, they can attract positively charged species in solution. On the contrary, groups such as amine, amide or imidazole are positively charge when protonated and neutral when deprotonated, so at pH values lower than the pK of those chemical groups the attraction of negatively charged species is favoured.

Since protons are always present in solution, the study of proton binding to biosorbents and its dependence on pH, ionic strength and medium composition should constitute the first step in any biosorption study.

Besides, competitive adsorption effects and biomass adsorption capacity are also related to the acid-base properties of the biosorbent. Despite its critical importance, few authors have included a systematic investigation of the acid-base properties of biomass in their biosorption studies (Bouanda et al. 2002; Li and Englezos 2005; Liu et al. 2013; Martín-Lara et al. 2008; Ravat et al. 2000; Rey-Castro et al. 2003; Schiewer and Volesky 1997a; Vilar et al. 2009). A simple bibliographic search using Scopus and Web of Science databases shows that <3% of the total peer-reviewed literature contain any of the key words related to acid-base studies when searching for “biosorption” or “biosorbent” (**Fig. *1***).

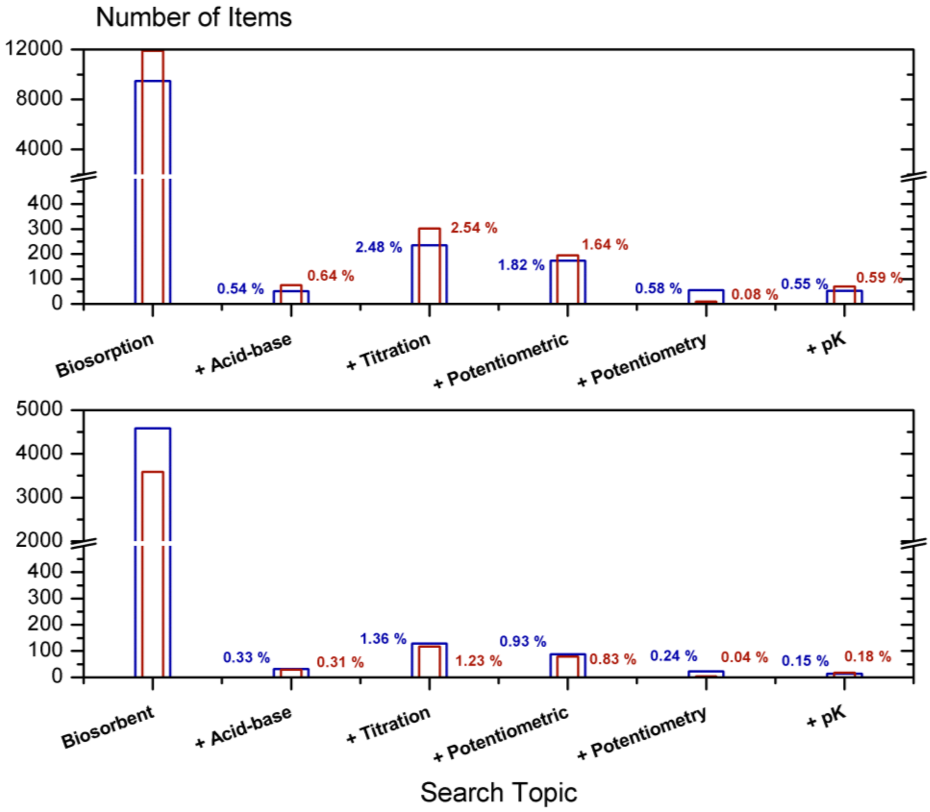

Fig. 1 Total bibliography search scores (January 2018) using Scopus (blue bars) and Web of Science (red bars) databases for “biosorption” and “biosorbent”, containing any of the key words related to acid-base studies: acid-base, titration, potentiometric, potentiometry or pK. The figure shows that less than 3% of biosorption papers include studies on proton binding

The biosorbents present a high heterogeneity with a range of dissociation constants of their chemical groups (Volesky 2003). The heterogeneity together with the similarity in the equilibrium constant of the chemical groups, make the accurate experimental determination of specific contributions from each binding site a challenge (de Wit et al. 1993). An alternative to the experimental determination of proton binding constants consists in their semi-empirical estimation using Linear Free Energy Relationships (Matynia et al. 2010). This methodology has been used for natural organic matter (e.g. fulvic and humic compounds), including the determination of metal-ligand constants (Carbonaro et al. 2011).

The presence of light metals in solution influences the binding of other species (e.g. pollutants) competing for the same chemical sites. Typical “hard” counterions (Na, K, Mg, Ca) form electrostatic bounds with negatively charged chemical groups, and reduce the local concentration of other ions (e.g. protons and metals) until convergence with their concentration in the bulk solution. The electrostatically bound counterions cannot displace covalently bound ions, but can reduce their local concentration, and then also decrease the covalent binding. The ionic strength (I), a function of the concentration and charge of ions in solution, is therefore another key parameter, together with pH, to consider during biosorption studies. A medium of constant ionic strength is required to perform the potentiometric titration of biosorbents. The ionic strength does not influence the number of acidic groups obtained from an acid-base titration, but it strongly affects the apparent proton binding constant values of those chemical groups. Besides, the medium composition should also be considered during the calibration of the pH electrodes used on titration studies.

The main aim of this paper is to characterize the proton binding equilibria, as an extremely important and preliminary step, for a correct interpretation of biosorption results. We first investigate the basics of the acid-base properties of simple substances in saline solutions. This analysis will provide a proper interpretation of the more complex physicochemical behaviour of polyelectrolytes and biosorbents. We evaluate the role of key parameters such as the ionic strength, pH or medium composition. Following, we show and discuss what has been done so far regarding acid-base characterisation of biosorbents and what models have been commonly used to describe the proton binding equilibria. Moreover, the role that acid-base properties of biosorbents play on pollutant removal is also discussed. Finally, we propose some experimental considerations for future works that cover all issues concerning the acid-base studies of biosorbents.

It is worth mentioning that for the sake of simplicity most of the discussions and analysis shown here are focused on the acid-base properties of biosorbents and their implications for metal biosorption. Nevertheless, proton binding also influences the biosorption of other pollutants such as organic compounds. The basic interaction principles are similar for either metals or organic substances. Moreover, most of the theoretical and practical considerations described in this paper allow for the description of the biosorption of any pollutant. However, the extrapolation of the results and models considered here to pollutants other than metals should be considered cautiously.

This article is an abridged version of the chapter published by Lodeiro et al. (2018) (Lodeiro et al. 2018) in the series Environmental Chemistry for a Sustainable World (https://www.springer.com/series/11480).

2. Acid-base properties in solution: pH, ionic strength and medium composition as relevant variables

Organic functional groups are part of the polysaccharides that form the structure of the biosorbents. The study of the acid-base properties of these simple compounds is therefore of great importance.

Considering the dissociation of an acid, AH, in aqueous solution (Eq. 1) different operational equilibrium constants can be defined:

$$AH \leftrightarrows A^- + H^+ \tag{1}$$

$$K^T = \frac{(A^-)(H^+)}{(AH)} = \frac{[A^-][H^+]}{[AH]} \frac{\gamma_{A^-}\gamma_{H^+}}{\gamma_{AH}} = K^* \frac{\gamma_{A^-}\gamma_{H^+}}{\gamma_{AH}} \tag{2}$$

where K^T and K^* are the thermodynamic and stoichiometric proton dissociation constants, respectively; the brackets represent activities, the square brackets represent concentrations, and γ_i are the activity coefficients.

While the thermodynamic proton dissociation constant depends on pressure, temperature and solvent, the stoichiometric one is also dependent on the medium composition: ionic strength and electrolyte type. As described in Eqs. *2*-3, this dependency is a function of the activity coefficients of the species involved, which are ions and neutral molecules:

$$K^T(P, T, solvent) = K^* \cdot Q(\gamma_i) \tag{3}$$

where $Q(\gamma_i)$ represents the ratio of activity coefficients of the species involved in the equilibrium. The activity coefficients are considered unity at infinite dilution or zero ionic strength.

Taking into account that activity coefficients in saline solutions can be expressed as a function of the ionic strength and the specific parameters of the system (Pitzer 1991), the following equation is obtained at constant P, T and background electrolyte (Daniele et al. 1997; Sastre De Vicente 1997):

$$pK^{*} = pK^{T} + f(I, system\ parameters) \quad 4$$

The representation of pK* *versus* ionic strength depends on the electrostatics involved in the acid-base equilibrium (Herrero et al. 1993). Therefore, in a typical ionization (charge separation) equilibrium (Eq. 1), a plot of the pK* dependence on ionic strength commonly passes through a minimum (Barriada et al. 2000). Nevertheless, the pK* is usually a linear function of the ionic strength when isocoulombic equilibria are involved (Herrero et al. 1992); this is commonly observed, for example, for amine protonation reactions: $BH^{+} \leftrightharpoons B + H^{+}$. An example of these two behaviours can be seen in **Fig. *2***.

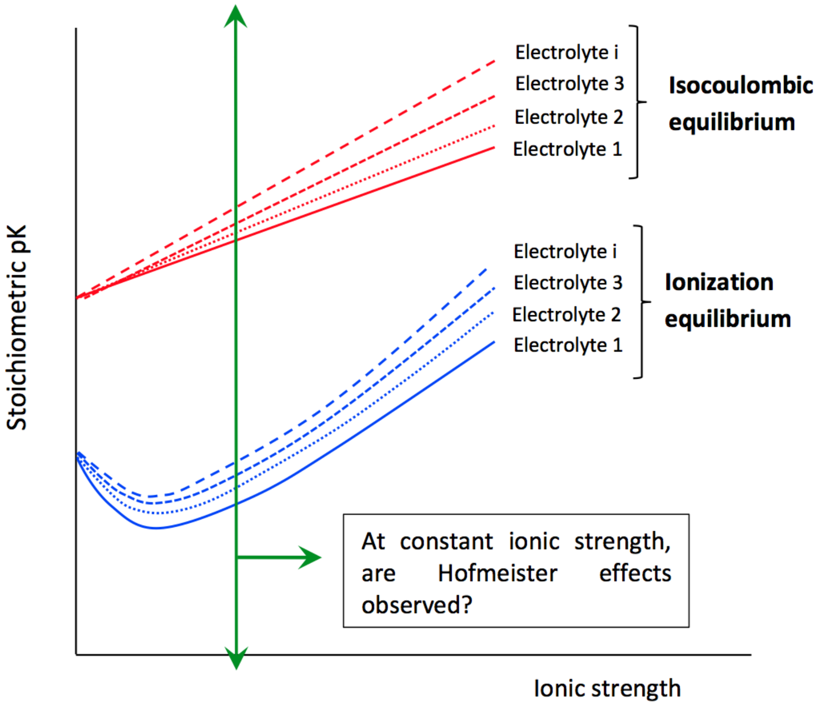

Fig. 2 pK* *versus* ionic strength plot for isocoulombic and ionization acid-base equilibrium. For isocoulombic equilibria, pK* is a linear function of the ionic strength (red lines). On the contrary, the plot shows that for ionization

equilibrium, curves pass through a minimum (blue lines). Hofmeister effects could be identified at constant ionic strength

2.1 Models for the activity coefficients of species in solution

Different equations have been proposed to obtain expressions for the activity coefficients (log γ_i) according to the theory of electrolytes (Pitzer 1991). The activity coefficient of an electrolyte can be split into two contributions: long-range Coulomb's interactions and short-range specific interactions. The former are a function of the ionic strength, and are independent of the electrolyte nature. On the other hand, the short range interactions represent pairwise or three particle interactions in solution, hence they are electrolyte dependent. Most of the models used to calculate activity coefficients in electrolyte systems are based on the Debye-Hückel limiting law, which is only valid for very dilute concentrations i.e. <0.001 mol Kg^{-1}. This model considers that the interactions between ions are exclusively electrostatic, that is dependent on ionic strength. Equations that extend the validity range of activity coefficient calculations to moderate or high ionic concentrations should take into account not only the ionic strength, but also electrolyte specific effects. Different approaches have been proposed to account for non-electrostatic interactions between ions. The simplest models are based on the Specific Interaction Theory (SIT) of BrØnsted-Guggenheim, e.g. the Pitzer´s equations are a representative example (Pitzer 1991). The Pitzer formulation has been extensively used in the literature for different ligands in simple electrolytes and complex mixtures, such as seawater (Daniele et al. 1997; De Stefano et al. 2002; Grenthe 2002; Millero and Pierrot 2002; Turner et al. 2016). A more elaborate theory, the Mean Spherical Approximation (MSA), allows the calculation of the activity coefficients term, Q(γ_i), including explicitly the ion charge, size and concentration, and the temperature, as parameters in its formulation (Blum 1975). Therefore, the MSA theory allows, for example, studying size effects on chemical equilibria, which is not possible using Specific Interaction Theory expressions (Sastre de Vicente and Vilariño 2002; Vilarino and Sastre de Vicente 1996).

3. Gibbs free energy of proton binding: electrostatic and non-electrostatic contributions

About forty years ago, in a yet classical work on ionizable surfaces, Healy and White (Healy and White 1978) presented a reaction of dissociation as:

$$AH^{(Q-1)^-} \rightleftarrows A^{Q^-} + H^+ \qquad 5$$

For this dissociation process, or its thermodynamically equivalent proton adsorption/binding reaction, the interaction free energy can be split into two: on the one hand an electrostatic term associated with double layer interactions, on the other, contributions including dispersion and other non-electrostatic forces. The Gibbs free energy in adsorption processes usually involves a wide range of reaction energies, which can be grouped, as a first approximation, into non-electrostatic and electrostatic terms (Moreno-Castilla 2004):

$$\Delta G_{diss} = \Delta G_{non-elec} + \Delta G_{elec} \qquad 6$$

In addition, according to Van Oss (Van Oss 2006; Van Oss and Giese 2011), the ΔG_{diss} (dissociation) of interactions between two different entities e.g. molecules, particles and surfaces in aqueous solution can be expressed as:

$$\Delta G_{diss} = \Delta G^{LW} + \Delta G^{AB} + \Delta G_{elec} \qquad 7$$

where ΔG^{LW} and ΔG^{AB} represent Lifshitz-van der Waals and Lewis Acid-Base (including hydrogen bonding) energies, respectively (Goss and Schwarzenbach 2001). Both free energy terms can be either attractive or repulsive. The comparison of Eqs. *6* and *7* allows the identification of the relevant contributions of non-covalent interactions in the $\Delta G_{non-elec}$ term, also called intrinsic free energy (ΔG_{int}).

The protons are a master variable that controls any acid-base system and influences practically all processes in aqueous chemistry (Stumm and Morgan 1996). The pH, as discussed in section 2, becomes therefore an extremely important parameter affecting the proportion of neutral/charged sites in an adsorbent. This effect appears irrespective to the presence of metals or other substances in solution. Therefore, the pH also affects the interactions involved in the different Gibbs free energy contributions (Eq. *7*). In addition, other parameters such as the ionic strength, and the specific electrolyte nature, influence the energetic terms in Eq. *7* to a variable degree.

Therefore, for a given couple sorbent/sorbate in aqueous solution, the Gibbs free energy of adsorption (ΔG_{ads}) can be expressed as:

$$\Delta G_{ads} = \Delta G_{ads}(pH, I, electrolyte\ nature) \tag{8}$$

The pH and ionic strength are generic variables independent of the characteristic of the electrolytes present in solution, and both contribute to ΔG_{elec}. These variables modulate the electrical properties of the interface sorbate-solution/sorbent, acting as a sort of charge regulators (Trefalt et al. 2016). Moreover, the influence of the nature of dissolved salts in solution is associated to Hofmeister lyotropic or salting in *versus* salting out effects.

Those terms are widely used to describe specific electrolyte effects on many physicochemical properties (Salis and Ninham 2014).

Equation *7* is a general expression that can be applied to adsorption processes involving different sorbates, e.g. protons, metals or organic substances, with distinct speciation characteristics and variable structural complexity, i.e. different polarity or charge, degree of hydrophobicity, etc.

Equations *7* and *8* also indicate that changes in the pH, ionic strength and/or the nature of salts in solution, will affect the value of ΔG_{ads}. Therefore, in order to properly understand dissociation/binding reactions, different experiments at several pHs, ionic strengths and/or electrolyte types should be performed. An adequate interpretation of the obtained results leads to important physicochemical information of the process such as intrinsic equilibrium constants. However, in most cases data interpretation involves the use of different models. Besides, when modelling data, specific physical properties of the adsorbent/biomass e.g. volume, size, texture, etc. are required or assumed.

4. Modelling the proton binding equilibria in biosorbents

The following discussion is based on the split of the adsorption energy into electrostatic and other non-electrostatic contributions proposed in Eq. *6*. This division allows simplifying and correctly interpreting the proton binding equilibria in biosorption processes under different experimental conditions.

4.1 Electrostatic effects: Influence of pH and ionic strength

In most cases, the biosorbents present a negative charge associated to the dissociation of their acidic groups. One of the main differences in studying the acid-base properties of simple organic ligands and biosorbents is due to the higher charge associated with the latter (polyelectrolyte effect). Moreover, the interactions of biosorbents with other species such as metals or organics in solution depend on the acid-base properties of the biomass and the chemical speciation. Therefore, the study of variables such as the pH, ionic strength or sorbate/binding-sites ratio is of great importance. These variables regulate the relative significance of the observed effects, mainly those associated with electrostatic interactions.

As discussed in section 3, a simple way to model coulombic effects of proton binding to biosorbents consists of splitting the intrinsic (non-electrostatic) and electrostatic energy contributions to the binding according to Eq. *6*. The biosorbents contain natural biopolymers; considering therefore the biosorbent as a polyelectrolyte, the electrostatic work involved in bringing a proton from the bulk solution to the binding site can be written as (Morel and Hering 1993):

$$\Delta G_{elec} = nF\psi_0 = F\psi_0 \tag{9}$$

where *F* is the Faraday constant and ψ_0 is the electrostatic potential at the location of the binding site. In terms of equilibrium constants, the equation reads:

$$K_{elec} = e^{-\frac{\Delta G_{elec}}{RT}} = e^{-\frac{F\psi_0}{RT}} \tag{10}$$

Considering the proton dissociation reaction presented in Eq. 5, a biosorbent of charge *Q* will present an apparent dissociation constant (K_{app}) given by:

$$K_{app} = \frac{[A^{Q^-}][H^+]}{[AH^{(Q-1)^-}]} = \frac{(A^{Q^-})(H^+)}{(AH^{(Q-1)^-})}\frac{\gamma_{AH^{(Q-1)^-}}}{\gamma_{A^{Q^-}}\gamma_{H^+}} = K_{int}\frac{\gamma_{AH^{(Q-1)^-}}}{\gamma_{A^{Q^-}}\gamma_{H^+}} \tag{11}$$

The proton and ratio of the biosorbent activity coefficients correspond then to the corrections to the intrinsic dissociation constant, K_{int}. If Q>>>1, the following effective activity coefficient can be defined as (Morel and Hering 1993):

$$ln\,\gamma_{eff} = ln\frac{\gamma_{A^{Q^-}}}{\gamma_{AH^{(Q-1)^-}}} = -\frac{F\psi_0}{RT} \tag{12}$$

The intrinsic dissociation constant can be calculated from:

$$K_{int} = K_{app}\gamma_{H^+}\gamma_{eff} = \frac{[A^{Q^-}]}{[AH^{(Q-1)^-}]}(H^+)_0 \tag{13}$$

The local ion activity of the proton at the binding site, $(H^+)_0$, is then given by its experimentally accessible bulk activity, (H^+), multiplied by a Boltzmann factor:

$$(H^+)_0 = [H^+]\gamma_{H^+}e^{-\frac{F\psi_0}{RT}} = (H^+)e^{-\frac{F\psi_0}{RT}} \tag{14}$$

Therefore, the surface proton activity, $(H^+)_0$, or concentration can be obtained from the electrostatic potential at the active binding site. The value of the electrostatic potential can be estimated using different models, as shown below. When considering the proton activity, but not the concentration, a correction for the activity coefficient of the proton in solution is required. Therefore, a suitable model for the activity coefficient (Pitzer 1991) should be chosen depending on experimental conditions, especially at low or high ionic strengths.

In addition to geometrical constraints, the potential around a charged species in an electrolyte solution is a function of the ionic strength. Equation *14* constitutes the basis for carrying out electrostatic corrections, which present different dependencies on ionic strength.

The presence of an electrolyte in solution can affect the binding in a direct and indirect way. The former reduces the occurrence of other ions near the binding sites, while the indirect way is due to the fact that intraparticle activities are higher than bulk activities. Nevertheless, according to the interpretation and definition of the Debye length, it is worth mentioning that in most cases electrostatic effects should be suppressed at ionic strengths c.a. 0.5-1 mol Kg^{-1} (Israelachvili 2011). However, a minimum in the Debye length has been observed around these values for some systems (Smith et al. 2016).

By analogy with models initially developed for humic and fulvic acids (Saito et al. 2005), two different approaches have been mainly used to account for electrostatic effects in biosorbents, namely one and two phase models (**Fig. *3***). Two-phase models consider the active polyelectrolyte (biosorbent) sites as a three-dimensional permeable structure or Donnan volume; while in one-phase models an active rigid surface (two-dimensional double-layer) is assumed. Calculating the contribution of electrostatic effects to free energies usually involves solving the appropriate Poisson-Boltzmann equation (Eq. 15), which relates the Laplacian of the electrostatic potential (ψ) to the charge density in the medium (Bartschat et al. 1992).

$$\nabla^2\psi = -\frac{1000F}{\varepsilon}\left(\sum_i z_i[X_i]e^{-\frac{F\psi}{RT}} + \rho_0\right) \tag{15}$$

where ρ_0 (mol·L^{-1}) is the charge in the region occupied by the biosorbent in the absence of mobile ions, and the summation term is the charge density produced by the distribution of co- and counterions (X_i) in the potential field. Equation *15* is valid either for surface double-layer (ρ_0= 0) or Donnan models, where $\rho_0 \neq 0$.

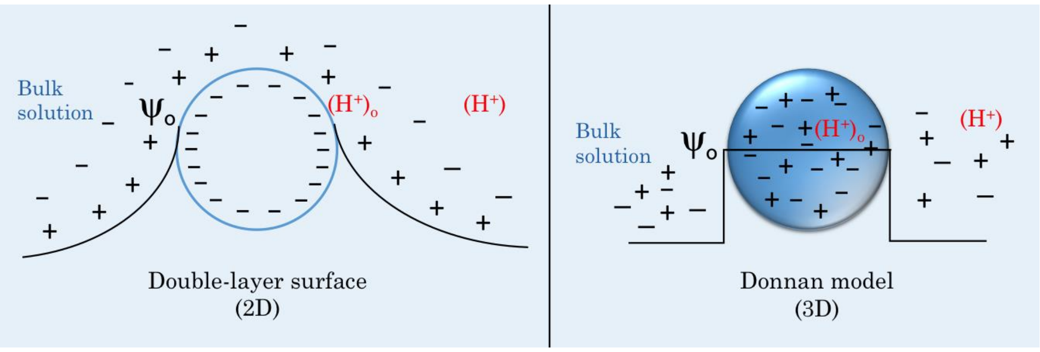

Fig. 3 Schematic representation of the double layer surface model (left panel) and Donnan model (right panel). The former considers the active binding sites as a two-dimensional rigid structure. On the contrary, on the later the active sites are represented as a three-dimensional permeable volume.

The Surface Complexation Model (SCM) is one of the most well-known and used surface models. The works of Borrok *et al.* (Borrok et al. 2005) and Goldberg *et al.* (Goldberg and Criscenti 2008) constitute a good review for this matter. Table *1* shows several examples for biosorption of brown algae; for these biosorbents the Donnan model is often applied. A more extensive table, including other types of algae and other biomaterials can be found in (Lodeiro et al. 2018). It is worth mentioning that most of the references shown in Table *1* do not include any ionic strength (electrostatic) correction term when analysing the proton binding. Moreover, significant differences can be found regarding important experimental conditions, such as the electrode calibration or the ionic strength adjustment during the proton titration performed by different authors.

A suitable model describing the electrostatic contribution to the binding has to be based on the biosorbent properties. The Donnan-type models are applied when the biosorbent has a permeable structure that shrinks and swells, its size is larger than the double-layer or Debye thickness and presents a large surface charge uniformly distributed within the biomass. Those characteristics are typical, for example, of many marine algae (Pagnanelli et al. 2004; Rey-Castro et al. 2004a; Rey-Castro et al. 2003; Schiewer 1999; Schiewer and Volesky 1997a; Schiewer and Volesky 1997b; Schiewer and Wong 2000), and lignocellulosic agriculture derivatives (Bouanda et al. 2002; Lopez et al. 2011; Zhao et al. 2015). On the contrary, the SCM is used when the adsorbent is considered to have an impenetrable, rigid surface; for example, surface complexation models have been used to describe metal and proton binding on bacterial surfaces (Borrok and Fein 2005; Fein et al. 2005; Fein et al. 1997; Grenthe 2002; Haas 2004; Leone et al. 2007; Liu et al. 2013; Ngwenya et al. 2009). Despite the different structural considerations on which those models are based, fitting similarities between Donnan and double-layer surface models have been reported when describing experimental binding data (De Stefano et al. 2005; Rey-Castro et al. 2004a; Rey-Castro et al. 2004b). In fact, Donnan models have been successfully applied to bacterial biomass (Burnett et al. 2006; He et al. 2013; Heinrich et al. 2007; Martinez et al. 2002; Pagnanelli et al. 2004; Plette et al. 1995; Yee et al. 2004), and double layer models to agriculture derivatives (Ravat et al. 2000; Reddad et al. 2002) or algae biomass (Kim et al. 1998).

The master curve approach is used to obtain a validation test of the electrostatic model used to describe the charged biosorbent. This approach consists on performing potentiometric titrations against a simple ion, usually the proton, in an electrolyte solution at different ionic strengths (see Fig. *4*). Therefore, the proton binding data, obtained from experimental titrations, can be transformed using the electroneutrality condition into data of net charge

(Q), proton coverage or dissociation degree of the biosorbent *versus* pH (see section 6 for details).

Table 1. Compilation of potentiometric experiments for different brown algae including experimental and modelling titration conditions.

Biosorbent	**Electrostatic proton binding model**	**Specific Interaction Model**	**Master Curve approach**	**Chemical proton binding model**	**Electrode Calibration**	**pH range**	**Ionic strength mol/L**	**Electrolyte**	**Reference**
Brown algae	Donnan/ Diffuse layer	Pitzer/No	Yes	Continuous (L-F)	Proton concentration	2–10/11.5	0.05–2	NaCl and KNO_3	(Rey-Castro et al. 2004b; Rey-Castro et al. 2003)
Brown algae	No	No	No	Discrete (one site)/ Continuous (L-F)/ Katchalsky	Proton concentration	2.2–6.5/11	0.05	$NaNO_3$	(Lodeiro et al. 2006a; Lodeiro et al. 2005a; Lodeiro et al. 2004; Lodeiro et al. 2005b)
Brown algae	No	No	No	No	No info	3–10	0.001	NaCl	(Fourest and Volesky 1997)
Brown algae	No	No	No	Discrete	No info	2.5–4.5	0.1	$NaNO_3$	(Seki and Suzuki

				(one site)					1998)
S. Polycystum (brown alga)	No	Davies equation	No	Discrete (three sites)	No info	2–10.5	0.1 and 1	$LiNO_3$	(Yun 2004; Yun and Volesky 2003)
Sargassum sp. (brown alga)	Donnan	No	No/ pH-pNa	Discrete (one site)	No info	2–6	0–1	$NaNO_3$	(Schiewer and Volesky 1997b)
S. fluitans (brown alga)	Donnan/CHEM model	No	No	Discrete (one site)	No info	2.2–4	0–5	$NaNO_3$	(Schiewer 1999)
S. fluitans (brown alga)	No	No	No	No	No info	3–10	0.001	NaCl	(Fourest and Volesky 1996)
Brown/green algae	Donnan	No	No	Discrete (one site)	No info	2–8.5	0–0.1	Deionised water/ $NaNO_3$	(Schiewer and Wong 2000)
P. caniculata (brown alga)	No	No	No	Discrete (two sites)-Continuous Sips (L-F)	Buffers pH 4, 7 and 10	2.5–9.5	0.001–0.1	$CaCl_2$	(Costa et al. 2010)

As stated in the previous section, the pH and ionic strength modulate the net charge of the biosorbent, then:

$$Net\ charge = function(pH, I) = function_b(pH_0) \tag{16}$$

where pH_0 (-log $[H^+]_0\gamma_{H+}$), the pH at the local binding site, can be obtained from Eq. 14.

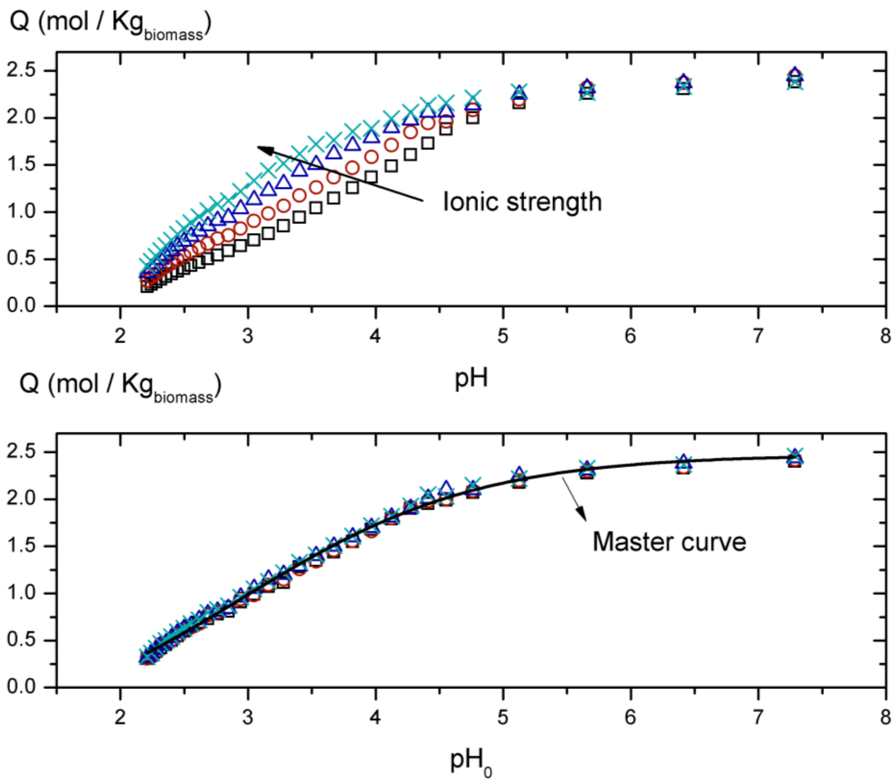

Fig. 4 Simulated data of charge *versus* pH curves (top graph) and calculated master curve (bottom graph) in a specific electrolyte solution. The master curve approach is built on the electroneutrality condition, so the proton binding data can be transformed into data of net charge. If the electrostatic model is correct, the dependence of the binding on ionic strength vanishes; therefore, the corrected binding curves merge into the master curve that is independent of the ionic strength as it can be observed in the bottom graph

Therefore, the charge-pH curves obtained over a range of ionic strength are used to optimise the parameters of the selected electrostatic model. If the electrostatic model used to calculate ψ is correct, the dependence of the binding on ionic strength should vanish and the corrected binding curves will merge into the so-called master curve that is independent of the ionic strength (Eq. 16).

More advanced theoretical treatments based on Monte Carlo simulations allow the study of potentiometric titration of ionizable polyelectrolytes (Madurga et al. 2009) , not only on the influence of the ionic strength but also on the effect of ion size and surface charge models.

4.2 Non-electrostatic (intrinsic) effects: Hofmeister series

Electrostatic interactions alone cannot provide with an explanation of ion-specific interactions and their associated outcomes. This is because pure electrostatic treatments predict that ions of the same valence provide the same results, irrespective of their chemical nature. The so-called non-electrostatic or intrinsic effects are associated to specific ion or salt effects in solutions or interfaces of different electrolytes. The intrinsic effects are involved in many phenomena including colloid, polymer and interface science in the fields of chemistry or biology (Cacace et al. 1997; Lo Nostro and Ninham 2012).

Franz Hofmeister was a pioneer of specific salts effects with his work on the precipitation of proteins (Kunz et al. 2004a). These non-electrostatic interactions or dispersion forces are associated to the specific nature of ions, their size and their polarizability. These effects, represented by the terms ΔG^{LW} and ΔG^{AB} in Eq. 7 are interpreted as differences in the properties of salts in solution, usually at concentrations higher than 0.1 M (Ninham and Yaminsky 1997). Dispersion forces as a whole have a relevant role. Nevertheless, their analysis through theoretical developments is challenging.

From a theoretical point of view, the electrostatic and dispersion forces must be equally treated. One of the current approaches consists of including an additional term of dispersion, which is added to the conventional electrostatic potential, in the Poisson-Boltzmann equation. The ionic distribution at an interface is given then by (Kunz et al. 2004b; Parsons et al. 2011; Salis and Ninham 2014):

$$c_{\pm} = ce^{\pm\frac{(z_i e\psi + U_{\pm})}{kT}} \quad 17$$

Therefore, the Eq. 14 that describes the proton activity at the local binding site would be also modified including an energetic dispersion-dependent term ($U_{\pm}$), thus providing a more realistic picture of the forces involved.

Quantitative studies on Hofmeister effects are scarce (Parsons 2016), and most works rely on qualitative or semi-quantitative analysis of results. Most of these papers are particularly focused on the adsorption of organic substances (Nelson and Schwartz 2013; Para and Warszynski 2007) where the complexity of electrostatic and non-electrostatic interactions is always present (Bauerlein et al. 2012). Some recent simulation studies on ion binding to carboxylic groups considering Hofmeister effects have also been performed (Schwierz et al. 2015; Stevens and Rempe 2016). These studies are of interest for biosorption due to the relevance of the carboxylic groups, which usually form part of the polysaccharide structure in many types of biomasses.

Despite pH or ionic strength effects that are studied in biosorption, to the best of our knowledge, there are no studies related to specific salt or Hofmeister effects.

4.3 Empirical models to describe the proton binding in biosorbents

The complex and heterogeneous nature of biosorbents makes the investigation and interpretation of their acid-base properties challenging. The local binding interface is supposed to be constituted of a charged polyelectrolyte. Therefore, the proton dissociation of an acid group in a biosorbent can be described using a reaction formally identical to Eq. *1* but considering AH as a whole (not only a specific acid site). The apparent conditional dissociation constant (K_{app}) can be written then as:

$$pK_{app} = pH - \log\frac{\alpha}{1-\alpha} \qquad 18$$

where the degree of dissociation, α, is given by:

$$\alpha = \frac{[A^-]}{[A^-]+[AH]} \qquad 19$$

Ideally, as previously mentioned, the relative contribution from each of the effects concerning equilibrium binding in biosorbents should be accounted for by means of an appropriate model.

A first approach, suggested in several biosorption studies, is to fit the potentiometric titration data with a set of previously defined discrete ligand constants. A further approach involves the use of a Gaussian distribution of ion binding constants, considering the well-known heterogeneity of the biosorbents. Despite the simplicity of those models, they can provide useful information regarding the acid-base and complexation equilibria under specific conditions of pH, ionic strength, temperature and medium composition. Nevertheless, these empirical models fail when relating the specific properties of biosorbents, such as size or charge distribution, to the model fit parameters.

In the majority of cases, the equilibrium constants determined in biosorption studies are conditional stoichiometric constants, K^* (see Eq. *2*), valid only for the specific ionic strength at which they have been determined. These conditional constants indirectly include all unspecific interactions among ions, namely, activity coefficients.

The modified Henderson-Hasselbach equation (Eq. 20) is one of the empirical models widely used to describe the dependence of the protonation constants of polyelectrolytes or biosorbents on the degree of dissociation:

$$pH = pK_m + n\, log\frac{\alpha}{1-\alpha} \qquad 20$$

where pK_m and n are empirical constants that change with ionic strength. Therefore, the relationships between pK_{app} and α or pH can be easily obtained:

$$pK_{app} = pK_m - (n-1)\, log\frac{\alpha}{1-\alpha} \qquad 21$$

$$pK_{app} = pK_m - \left(\frac{n-1}{n}\right) pH \qquad 22$$

Note that pK_m=pK_{app} for α=0.5 and n>1. Potentiometric titrations of biosorbents do not provide a simple set of discrete dissociation constants, as when using simple ligands, but a continuous distribution of binding sites. This fact, together with the polyelectrolyte and associated effects, results in flatter titration curves with not well-defined end points.

The best description of the binding properties of biosorbents has been provided therefore, when the model explicitly includes both, heterogeneity and polyelectrolytic effects (despite conformational changes, not explicitly reflected). Therefore, reorganising Eq. 14 and substituting in Eq. 18 provides with an expression for the solution pH (-log $[H^+]\gamma_{H+}$) or pK_{app}:

$$pH = pK_{int} + log\left(\frac{\alpha}{1-\alpha}\right) - \frac{1}{ln10}\frac{e\psi_0}{kT} \qquad 23$$

$$pK_{app} = pK_{int} - \frac{1}{ln10}\frac{e\psi_0}{kT} \tag{24}$$

It is worth mentioning that on the Donnan and surface charge models pK_{int} refers to the limit of high ionic strength, where ψ tends to zero, as the reference state. Nevertheless, for simple ligands the ion activity coefficients, so the pK_{int}, are referred to zero ionic strength or infinite dilution, where no interactions between ions are assumed. It is therefore important to consider this difference when comparing intrinsic binding constants of polyelectrolytes or biosorbents with the ones obtained for simple ligands. Moreover, for simple ligands, the Debye-Hückel law imposes a proportional dependence of pK with $\sqrt{I}$ at low ionic strengths, whereas for a biosorbent or polyelectrolyte an approximately linear increase of pK with log I is expected as the ionic strength decreases.

4.4 Description of the chemical heterogeneity

Once the electrostatic and/or non-electrostatic effects have been explicitly accounted for, a set of intrinsic binding constants that only depend on the chemical heterogeneity can be obtained. The biosorbents present many different chemical groups that can also have different steric and chemical environments. Therefore, a model for the description of the chemical heterogeneity is required. For the particular case of proton binding reactions, the coverage fraction of binding sites (θ) is given by:

$$\theta = 1 - \alpha = \frac{[AH]}{[A_{tot}]} = \frac{[AH]}{[A^-] + [AH]} \tag{25}$$

The plot of θ *vs* [H$^+$] is called the binding curve. The models used to account for chemical heterogeneity usually describe the coverage fraction of binding sites as a weighted sum of local isotherms (*f*), which describe the binding in each site. If it is assumed that the binding sites do not interact each other, and all have the same local isotherm:

$$\theta([H^+]) = \int_0^\infty p(K) f([H^+], K) dK \tag{26}$$

where *p(K)* is a probability density function known as the affinity spectrum, which represents the fraction of binding sites with a value of the microscopic affinity constant between *K* and *K*+*dK*. The simple Langmuir or Langmuir-Freundlich equations are commonly used as local isotherms. Therefore, the proton affinity distribution can be calculated using a simplified approximation of the local isotherm by using, for example, the condensation approximation (CA) method. In this method, the local isotherm is replaced by a step function, which is the first derivative of the binding curve:

$$f_{CA}(log\, K = -\,log[H^+]) = \frac{d\theta}{d\, log[H^+]} \tag{27}$$

Alternatively, the experimental binding curve data can be described by means of an arbitrary empirical isotherm, using a conventional fitting procedure. The NICA (Non-Ideal Competitive and thermodynamically consistent Adsorption) isotherm model has been extensively used to describe heterogeneity and competition on ion binding to humic/fulvic substances (Kinniburgh et al. 1999) and many different biosorbents (Herrero et al. 2011; Lodeiro et al. 2006b; Lopez et al. 2011; Zhao et al. 2015). If only proton binding is considered (absence of competing ions) the NICA equation leads to the well know Langmuir-Freundlich isotherm.

On account of the importance of the ion exchange mechanism in biosorption, it is worth mentioning that analogies and differences between competitive adsorption models and ion exchange models has been discussed and analysed for metal biosorption systems, concluding that both descriptions are equivalent if only equilibrium properties are compared (Plazinski 2013; Rudzinski and Plazinski 2010). Moreover, heterogeneity effects considering a continuous function of binding site, the stoichiometry of the ion exchange reaction responsible for the “apparent” heterogeneity and a site discrete model, have also been studied (Plazinski and Rudzinski 2009; Plazinski and Rudzinski 2011).

5. The role of the acid-base properties of biosorbents on metals removal

This section is focused on some selected examples where the interactions of biomass with metals are described.

The relationship between the acid-base properties of biosorbents and their adsorption capacity is probably the key question in many biosorption studies. This issue is not a simple one because of the nature of biomass, which consists of a varied and complex mixture of polymeric species. However, the detailed investigation of acid-base properties reveals that the polymer in largest proportion determines the fundamental behaviour.

The analysis of the adsorption capacity is an even more complex issue, mostly because of the failure to elucidate the adsorption mechanism. Biosorption consist of several mechanisms (Chen and Wang 2009; Javanbakht et al. 2014) mainly physical adsorption, ionic exchange, complexation, chelation, reduction or microprecipitation (Crini 2005; Schiewer and Volesky 2000; Veglio and Beolchini 1997).

The interaction, and thus the adsorption, is strongly dependent on the solution conditions, which are decisive for the biomass surface, the metal speciation or the competition of other ions or organic molecules. The direct consequence is that it is difficult to explain the adsorption by one single mechanism. Therefore, it is quite possible that some of these mechanisms are acting to varying degrees simultaneously, most commonly, the ionic exchange, complexation, reduction/oxidation reactions and metal precipitation.

The occurrence of the functional groups involved in the ion exchange and complexation mechanisms are usually the same as those that account for acid-base properties. When these two mechanisms govern the adsorption, there is a direct correlation with the acid-base properties of the biomass (Schiewer and Volesky 1995).

When reduction of the metal ions and resulting metal precipitation play the key role, the adsorption is attributed to those functional groups that are easily oxidisable, without need for being related to the acid-base properties.

In any case, as indicated above, it is most likely to find a complex mechanism in which some of the above-mentioned processes participate simultaneously.

A large number of studies report the correlation of the adsorption capacity with the number of protonated groups in the biomass. Lodeiro et al. (Lodeiro et al. 2008) studied the Cr(III)-binding capacity of three different types of biomass, the brown *Sargassum muticum* macroalga, orange peel and bracken fern. On the one hand, the authors found that the maximum Cr(III) uptake capacity is approximately equal to the number of carboxyl functional groups determined by potentiometric measurements. On the other hand, the obtained complexation constants (log K_{Cr}=2.9-3.1) are very similar for the three materials studied, that reinforces the hypothesis of the implication of the same functional group, e.g. carboxyl groups, in metal uptake. Barriada et al.

(Barriada et al. 2009) studied the adsorption of Cd (II) and Pb (II) on bracken fern. Maximum uptake values were the same for both metals (0.410 mmol·g $^{-1}$), which is very similar to the number of acidic groups determined for this material (0.432 mmol·g $^{-1}$). Once again, the results indicate that acidic groups were responsible of the sequestration of both metal ions.

The analysis of the effect of pH on adsorption capacity provides further evidences of the implication of acidic groups on metal binding. For example, an S-Shaped curve centred at pH 3-4 is usually found for metal adsorption (Lodeiro et al. 2005a; Lodeiro et al. 2004; Ravat et al. 2000; Reddad et al. 2002; Schiewer and Volesky 1995). At pH values below c.a. 2.0, the metal uptake is very low, but not negligible, which is related to the presence of a relatively low amount of very strong acid groups such as sulfonic groups, which are present in the fucoidans of brown algae. The change in the ionic state of the carboxyl functional groups, which are associated with the polymers of the cell wall, explains the dramatic increase in adsorption of metals from pH 2 to 4. Above pH 4 the metal sorption capacity levels off at a maximum value (Haug and Smidsrod 1970; Rey-Castro et al. 2004a).

The fact that the same functional groups, i.e. the same sites, are used for the proton and metal binding is evident when acid-base and metal adsorption properties are modelled simultaneously, by use of competitive proton-metal models. The proposed equations are able to describe both proton and metal experimental data satisfactorily. Models of varying degrees of complexity have been proposed; some of them take into account different isothermal models, others several binding sites, heterogeneity or different stoichiometric proton/metal ratios.

Langmuir competitive model with a single binding site is one of the simplest models that has been successfully applied by Schiewer (Schiewer and Wong 1999) to Ni and Cu adsorption by several types of algae, assuming 1:2 binding stoichiometry. Lodeiro et al. (Lodeiro et al. 2005b) investigated the Cd adsorption by biomass of the brown marine algae *Sargassum muticum*. The authors compared Langmuir competitive models, assuming 1: 1 and 1: 2 stoichiometries. The NICA model can adequately explain all the experimental data, both concentration and pH dependence of cadmium uptake, employing the same constants obtained in proton binding studies. Pagnanelli et al (Pagnanelli et al. 2005) obtained similar results using the NICA model to reproduce the Cu and Cd biosorption experiments on olive pomace. Li and Englezos (Li and Englezos 2005) employed the NICA-Donnan model to describe the interaction of protons and metal ions, Cu (II), Pb (II), Fe (III) and Mn (II), and the lignin extracted from wheat bran and kraft pulp. They were able to reproduce with great accuracy the experimental data, assuming only two types of sites for the binding of protons or metal ions to lignin, considered to be due to carboxylic-type and phenolic-type groups.

Herrero et al. (Herrero et al. 2011) studied the Cu(II) uptake by the macroalga *Sargassum muticum*. A simple Langmuir or Langmuir-Freundlich isotherm can be used to accurately describe equilibrium experiments. However, only the NICA model allows a good description of all equilibrium experiments tested, i.e. isotherm, pH influence and competition between Cu and Cd, employing the same constants attained through proton binding studies.

All studies above make clear that protons and metal ions compete for the same adsorption positions on different types of biomass.

6. Potentiometric determination of the acid-base properties of biosorbents.

The determination of acid-base properties of the biosorbents provides very useful information about the physicochemical behaviour of these substances, and consequently their performance in adsorption processes. Not only the total number of acidic sites can be quantified, but also their proton binding affinities (Li et al. 2014; Pagnanelli et al. 2000; Pagnanelli et al. 2004; Schiewer and Patil 2008). However acid-base characterization is not limited to these two aspects, and it can also be used to determine the potential of zero charge (pzc) of the biosorbent (Fiol and Villaescusa 2009; Li et al. 2014; Lodeiro et al. 2012; Pagnanelli et al. 2013).

Broadly speaking, the determination of acid-base properties of biosorbents does not differ from the determination of the acid-base behaviour of any other simple substances. That is, during a titration a typical s-shape curve will be obtained, with one or several inflection points, depending on the nature of the biosorbent (Naja et al. 2005; Schiewer and Patil 2008). The analysis of these curves will provide the corresponding acid-base information of the substance under study. However, the analysis of the titration curves is not as trivial as that obtained for a single, pure substance (Lenoir and Manceau 2010). For biosorbents, the corresponding titration curves are not as sharp as the ones obtained for simple substances and the s-shape curves have inflection points not always well defined.

Different techniques can be used to obtain acid-base information of substances (Bouanda et al. 2002; De Stefano et al. 2005; Gans et al. 1996;

Gans et al. 2008), but potentiometry with glass electrode is the most important one, widely used especially in biosorbent acid-base analysis. Potentiometry requires very simple, commonly employed equipment present in any laboratory, and is also reasonably easy to automate (Barriada et al. 2009; Lodeiro et al. 2012; Lopez-Garcia et al. 2013), decreasing the manipulation of the sample and the preparation of different mixtures.

Potentiometric titrations are based in the measurement of the electromotive force (emf) appearing between a glass electrode and a reference electrode in a solution. In the case of a biosorbent determination, instead of working with a solution, a suspension of the biomaterial is present. As in any titration, the pH of the suspension is modified by addition of an acid or base, and the evolution of the pH of the mixture (or the emf readings) is followed. The pH or emf values and volume of titrant added constitute the starting data employed during analysis.

6.1 Experimental set-up

The typical potentiometric experiment set-up can be described as a vessel where the biosorbent suspension is allowed to attain equilibrium after each titrant addition (Barriada et al. 2009; Lodeiro et al. 2012; Lopez-Garcia et al. 2013). Temperature control using a thermostated vessel is particularly useful. The titration vessel is typically closed with a lid with several ports where the glass electrode, an inert gas bubbler and a tip for adding the titrant are introduced. A temperature probe is optional. A reference electrode is also required, but if just proton activity is going to be followed, a combination glass electrode is typically used. If other species activities are going to be measured (e.g. metal cations) a common reference electrode has to be shared between the glass electrode and the ion selective electrode in order to avoid reading interferences between the two electrodes. An inert gas bubbler must be used during the titration; it helps to remove the interference of gases present in the suspension, mainly CO_2 and O_2. A vigorous stirring procedure is often employed, typically magnetic stirring, to achieve a correct mixture of the suspension. However, caution with stirring has to be taken into consideration, since too vigorous stirring could disaggregate the biomaterial under study. This is especially important if high temperatures are going to be used during the titration.

Finally, another common procedure in potentiometric acid-base titrations, also for biomaterials, is the usage of an inert electrolyte (Barriada et al. 2009; Bouanda et al. 2002; De Stefano et al. 2005). A glass electrode is sensitive to proton activity, therefore in order to minimize the change in proton activity coefficient, a suspension of the biomaterial in a solution containing an inert electrolyte is employed rather than a suspension in pure water. Both the suspension of the biosorbent and the titrant added during the determination are prepared in a solution with the same ionic strength. This allows the response of the glass electrode to be related to the concentration of free protons in solution rather than to their activity. This procedure facilitates the subsequent derivation of the apparent equilibrium constants of the acidic groups involved in the acid-base equilibria.

6.2 Calibrations

When an inert electrolyte is present, the response of the electrode depends proportionally on proton concentration, while the activity coefficient of this species remains almost constant during the whole titration. In order to obtain a relationship between the proton concentration and the emf readings, a calibration procedure is followed. The simplest calibration can be performed using a solution of the inert electrolyte, where aliquots of a strong acid with electrolyte at the same ionic strength are added. If the concentration of the strong acid is accurately known, it is possible to calculate the concentration of the protons after each addition. A direct relationship between the emf readings and the proton concentration can be easily obtained using the following equation:

$$E = E^{*} + p\ log[H^{+}] \tag{28}$$

where E is the electromotive force, E* is the so-called formal potential. The slope in the representation, *p*, theoretically should be the Nernstian slope, 59.16 mV per decade in aqueous solutions at 25 °C. Nevertheless, in practice, it is considered a fitting parameter together with the formal potential. When a glass electrode is providing an accurate response, a plot of E vs. log $[H^+]$ renders a straight line (May et al. 1982) with a slope that should not be very different from the theoretical value. For every addition the concentration of protons is calculated as:

$$[H^{+}] = C_a \cdot \frac{v}{V_0 + v} \tag{29}$$

where C_a is the concentration of the acid in the titrant solution, v is the total volume of the aliquots of acid added for each emf reading and V_0 is the initial volume of the electrolyte solution.

Calculation of proton concentration for every addition using Eq. *29* together with the emf readings allow fitting of the experimental data to Eq. *28*, obtaining both the slope *p* and the formal potential.

Calibration of glass electrode following this procedure must be done periodically, since both formal potential and slope change over time

6.3 Measurements

A biosorbent titration is done with a suspension of the biosorbent. Therefore, a heterogeneous mixture is used rather than working with a homogenous solution. This fact makes stirring an important factor, since the biosorbent will tend to separate from solution by gravity. The time required to achieve a good hydration of the sorbent material is also important. In some cases, e.g. biomass from fern, the biomaterial is stored dry; when this material is used in a titration, it is quite water-repellent and it takes a considerable time to become fully hydrated. Other materials, such as alga, do not show this problem. They are hydrated within minutes, but they tend to swell and become very soft, so caution should be taken when stirring to avoid destruction of the sorbent.

Another point to take into consideration is the protonation state of the biosorbent; the functional groups that constitute the active sites of the material can be in different protonation states. A common procedure consists in doing an acid wash of the material in order to start the titration with the biosorbent on its fully protonated state (Barriada et al. 2009; Rey-Castro et al. 2003; Schiewer and Patil 2008). Other researchers have used a different approach. Starting with the native, untreated material, an accurate amount of acid is added to the suspension and the mixture is allowed to reach equilibrium (Pagnanelli et al. 2013). At that moment, the titration is started by adding base of known concentration. The amount of acid initially added is taken into account in the subsequent calculations.

It is also important to consider that during biomass titrations the glass electrode readings are much more unstable than in a common acid-base titration. Electromotive force tends to drift significantly, not only because a heterogeneous medium is involved, but also a complex biopolymer mixture is being titrated. Therefore, conformational modifications of the biomolecules can be expected during the titration besides complex electrostatic effects. Consequently, the titrations take a considerable time, and a criterion for "stable" readings must be adopted. Usually researchers considered that the glass electrode is "stable" if the change in the emf is small (below 1 mV) during a moderate time interval (2-5 min) (Bouanda et al. 2002; Naja et al. 2005). This drift in the readings is more significant when the titration is reaching an inflection point and a typical titration can take hours depending on the system under study. Since biomass titrations are time-consuming, automation of the titration is desirable. A computer controlled titration system can easily cope with the recording of experimental data that will be used in titration analysis (Barriada et al. 2009; Lodeiro et al. 2012).

6.4 Data analysis

The analysis of the data obtained during a titration is usually based on a charge balance equation: the charge of all the positive species has to be compensated by the charge of the negative species. Let us suppose that a titration of a biosorbent is done with sodium hydroxide and a known amount of hydrochloric acid has been added to start the titration in acidic conditions. In this situation, at any point of the titration the electroneutrality condition can be written as it follows:

$$[Na^+] + [H^+] - [Cl^-] - [OH^-] + Q = 0 \qquad 30$$

where Q is the charge concentration present in the biosorbent at each point of the titration. If the Q value is positive, it implies that the biosorbent has a neat positive charge. On the contrary, the biosorbent is negatively charged. The equation *30* can be easily transformed into charge-pH or master curves (see section 6).

If the glass electrode has been calibrated in the free proton scale, the emf readings can be easily transformed into proton concentration [H^+] (Eq. 28). Hydroxide concentration can be obtained from the equilibrium constant of water once the hydrogen concentration is known. The concentrations of sodium and chloride ions can be calculated from the concentration of the titrant, the initial volume of the mixture and the concentration of acid added. Therefore, the charge concentration of the biosorbent can be computed for each titrant addition.

If the charge is associated to an acidic group and the total number of groups is determined, the dissociation degree can be computed following Eq. 19 and the apparent dissociation constant can be obtained as it is described in section 4.3.

7. Conclusions and future research needs

a) A deep knowledge of the acid-base properties of biosorbents is the basis to understand the mechanisms of biosorption. Moreover, a full comprehension of basic acid-base processes helps to perform better the experimental set-up on biosorption studies. For example, the acid-base chemistry knowledge supports the design of biosorbents for a specific use, or the establishment of adequate experimental conditions for the optimum behaviour of a biosorbent.

b) Different external parameters have to be modified to obtain relevant information on the properties of the biosorbent. The most important variables at fixed temperature are the pH, the ionic strength and the nature of the electrolyte.

c) Ionization/protonation of biosorbents can be interpreted, as a first approach, in terms of Gibbs free energies including electrostatic and non-electrostatic interactions. This conceptual division allows associating the interaction terms with molecular parameters, which have relevant effects on the biosorption process. This approach is underdeveloped and future research is needed.

d) The analysis of possible Hofmeister series could help to quantify non-electrostatic effects associated with the interaction between biosorbent and adsorbate. The consideration of Hofmeister effects is not only valid for proton binding but also for interactions between biosorbents and other species such as metals or organic substances.

e) The proton is a master variable in aqueous chemistry that is involved in ion exchange, precipitation, complexation and other chemical processes. Proton experimental control is relatively easy by potentiometry. However, potentiometric measurements should be supplemented with other techniques that confirm the nature of the functional groups involved in the biosorbent acid-base behaviour.

f) The potentiometric technique also allows the determination of zero charge point values of the biosorbents. This aspect is well developed and discussed for minerals. Nevertheless, the interpretation and coherency of the values obtained for biomass materials is far from being clear. A systematic determination and investigation of zero charge values for biosorbents is therefore needed.

g) Basic interaction laws must be equal at different scales, although with unexpected effects. Therefore, the simple pH-metric technique should be also useful for the study and interpretation of the acid-base behaviour of nanosorbents. This use of potentiometry could provide with relevant information regarding acid-base properties of specific nanomaterials that should be considered for future studies.

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