Chapter 3
A Systematic Analysis and Review of the Fundamental Acid-Base 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. According to bibliography, less than 3% of biosorption papers include studies on proton binding. 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. This review 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 review concerning the acid-base properties of biosorbents. Only 30% of the reviewed papers that study algae, agricultural wastes or lignocellulosic materials use Donnan or double-layer surface models to account for electrostatic interactions on proton binding. Expressions for activity coefficients, such as Debye-Hückel or Pitzer equations, are shown only in c.a. 15% of these papers. Moreover, studies investigating a range of ionic strengths represent a 40%, while this variable is not even considered in 20% of the papers. We could not find any biosorption study related to specific salt or Hofmeister effects. Moreover, in 6 out of 10 papers there is important experimental information missing such as the calibration of the electrodes. We consider therefore that there is an important need for reviewing the role of proton binding on biosorption studies.

Symbols

A	Specific surface area
CA	Condensation approximation
$\mathrm{C_a}$	Concentration of acid solution
$\mathrm{C_A}$	Total concentration of acidic sites in a biosorbent
$c_{\pm}$	Ionic distribution at an interface
E^*	Formal potential
emf, E	Electromotive force
EXAFS	Extended X-ray absorption fine structure
F	Faraday constant, 96485.34 C mol^{-1}
f	Weighted sum of local isotherms
FTIR	Fourier transform infrared spectroscopy
$(H^+)_0$	Local proton ion activity at the binding site, e.g. surface proton ion activity
$[H^+]_0$	Proton ion concentration at the local binding site
(H^+)	Experimental accessible bulk activity of the proton ion
I	Ionic strength
K^*	Stoichiometric proton dissociation constant

K_{app}	Apparent conditional dissociation constant
K_{int}	Intrinsic dissociation constant
K^T	Thermodynamic proton dissociation constant
LFER	Linear free energy relationships
MSA	Mean spherical approximation
NICA	Non-ideal competitive and thermodynamically consistent adsorption
NMR	Nuclear magnetic resonance
NOM	Natural organic matter
pK_m	Empirical, ionic strength dependent pK
$p(K)$	Affinity spectrum
pzc	Potential of zero charge
Q	Charge of a species net charge
$Q(\gamma_i)$	Ratio of activity coefficients of the species in the equilibrium
SCM	Surface complexation model
SIT	Specific interaction theory
$U_\pm$	Dispersion-dependent energy term
v	Volume added in a titration
V_D	Active Donnan volume
V_0	Initial volume
WHAM	Windermere humic aqueous model
XANES	X-ray absorption near edge structure
X_i	Co-ions and counterions
z_i	Charge of a species
α	Degree of dissociation
$\gamma_\pm$	Mean ionic activity coefficient
γ_{eff}	Effective activity coefficient
γ_i	Activity coefficient of species i
ΔG	Gibbs free energy
ΔG^{AB}	Lewis acid-base contribution to Gibbs energy
ΔG_{ads}	Gibbs free energy of adsorption
ΔG_{diss}	Gibbs free energy in a dissociation equilibrium
ΔG_{elec}	Electrostatic Gibbs free energy
ΔG_{int}	Intrinsic Gibbs free energy
ΔG^{LW}	Lifshitz-van der Waals contribution to Gibbs energy
$\Delta G_{non-elec}$	Non-electrostatic Gibbs free energy
θ	Coverage fraction of binding sites
ρ_0	Charge in the region occupied by the biosorbent in the absence of mobile ions
σ	Charge density
Ψ	Electrostatic potential
Ψ_0	Electrostatic potential at the binding site

3.1 Introduction

The removal of pollutants (e.g. heavy metals, phenols, dyes, endocrine disruptors, etc.) from contaminated waters is an issue of current concern. 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 Convention for the Protection of the Marine Environment of the North-East Atlantic showed time trends for metals and organic contaminants in Europe during the period 2006–2011. For example, Cu, Zn and Pb show increasing trends in the majority of areas sampled; Hg and As trends are mainly descendent, while Cd does not show a clear trend (Larsen and Fryer 2012). The contribution of EU industry to pollutant emissions to water is substantial, with e.g. 36,875 kg for Cd, 498.2 tons for Pb and 1028.5 tons for phenols in 2010 (Lawton et al. 2014).

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.

Different representative definitions of biosorption with variable implications have been proposed in the last decade. Bohumil Volesky (2007) reported a broad definition in 2007 when biosorption was already a well-established technique: "*Biosorption has been defined as the property of certain biomolecules (or types of biomass) to bind and concentrate selected ions or other molecules from aqueous solutions. As opposed to a much more complex phenomenon of bioaccumulation based on active metabolic transport, biosorption by dead biomass (or by some molecules and/or their active groups) is passive and based mainly on the "affinity" between the (bio-) sorbent and sorbate*". B. Volesky included in his definition not only biomass but also biomolecules. Therefore, according to B. Volesky the accumulation of contaminants by polymers of biological origin, such as alginate or chitosan, should be considered as biosorption.

Later on Geoffrey M. Gadd (2009) pointed towards a wider biosorption definition including living and dead biomass: "*Thus, the term biosorption can describe any system where a sorbate (e.g. an atom, molecule, a molecular ion) interacts with a biosorbent (i.e. a solid surface of a biological matrix) resulting in an accumulation at the sorbate – biosorbent interface, and therefore a reduction in the solution sorbate concentration*". In contrast to the definitions generally suggested in literature (Volesky 2007; Michalak et al. 2013) both, passive and active accumulation of sorbates are implicitly included in Gadd's description.

More recently, I. Michalak et al. (2013) have proposed another representative definition of biosorption: "*Biosorption is a subcategory of adsorption, where the sorbent is a biological matrix. Biosorption is a process of rapid and reversible binding of ions from aqueous solutions onto functional groups that are present on the surface of biomass. This process is independent of cellular metabolism*". The distinction between biosorption and adsorption proposed by Michalak et al.

constitutes a novel aspect. Nevertheless, it is worth mentioning that biosorption is not only driven by adsorption but many other mechanisms such as ionic exchange, redox reactions, etc.

We suggest here a simple definition of biosorption as the removal of pollutants from solution using dead, non-metabolically active, biomass of biological origin (namely biosorbents), which preserve its pristine active chemical structure or active groups. We therefore consider that if the biomass is significantly processed, for example when preparing biochars by pyrolysis, the accumulation of sorbates involving those materials should not be defined as biosorption. Therefore, only papers that fit in the proposed definition of biosorption are reviewed here.

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 (Vijayaraghavan and Yun 2008a; Gupta and Diwan 2017), fungi (Kapoor and Viraraghavan 1995), agricultural by-products (Bhatnagar and Sillanpää 2010) or chitin and wood derivatives (Gerente et al. 2007; Abdolali et al. 2014). 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 biopolymers chains. It is therefore critical to understand the physicochemical properties of these natural polymers present in the biomass used in biosorption studies.

The knowledge about the biosorption mechanism is the base for proposing models, process understanding and experimental optimization. The biosorption mechanism is complex due to the heterogeneity and structure of the biosorbents (Aksu 2005; Robalds et al. 2016). Different chemical active compounds, 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 in solution. To understand the chemical nature of the biosorption process it is necessary to determine which chemical groups on the biosorbent are involved in the binding of different contaminants. 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. The dominant biosorption mechanisms usually proposed are: ionic exchange (Schiewer 1999), chemical binding (ionic and covalent) (Schiewer 1999) and redox reactions (Lopez-Garcia et al. 2013). Other phenomena, such as physical binding (electrostatic and van der Waals forces) or microprecipitation, may also have some contribution (Fiol and Villaescusa 2009). Those mechanisms can act in combination, with different contribution degrees, and even one binding site can participate in different binding mechanisms. For example, using algae as biosorbents, the proton binding has been considered to have a dominant covalent bound character at ionic strength > 0.1 mol kg^{-1} and above pH 3, while some electrostatic effects are noticed at lower ionic strength and pH < 3 (Rey-Castro et al. 2003). 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 (Dewit 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 (Fig. 3.1).

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 (Schiewer and Volesky 1997a; Ravat et al. 2000; Bouanda et al. 2002; Rey-Castro et al. 2003; Li and Englezos 2005; Martín-Lara et al. 2008; Vilar et al. 2009; Liu et al. 2013). 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. 3.2).

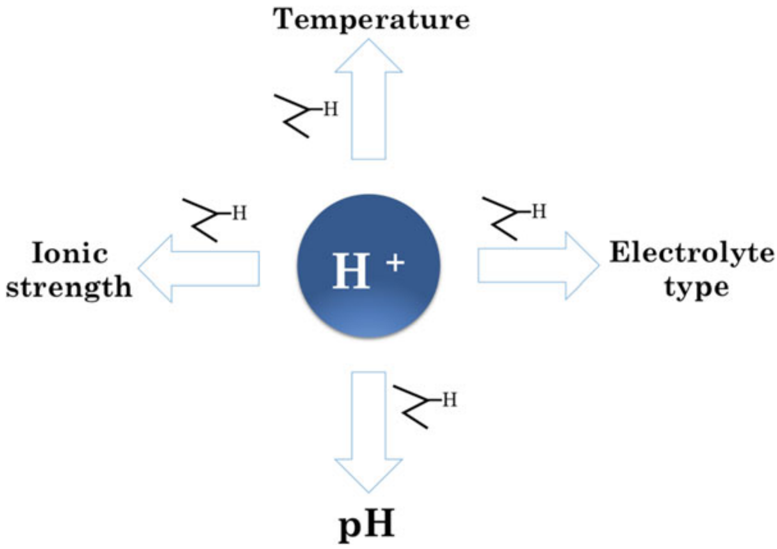

Fig. 3.1 Schematic representation of the main variables that affect proton binding to bioadsorbents. That is, ionic strength, pH, medium composition or electrolyte type, and temperature. In order to properly understand dissociation/binding reactions at constant temperature, different experiments at several pHs, ionic strengths and/or electrolyte types should be performed

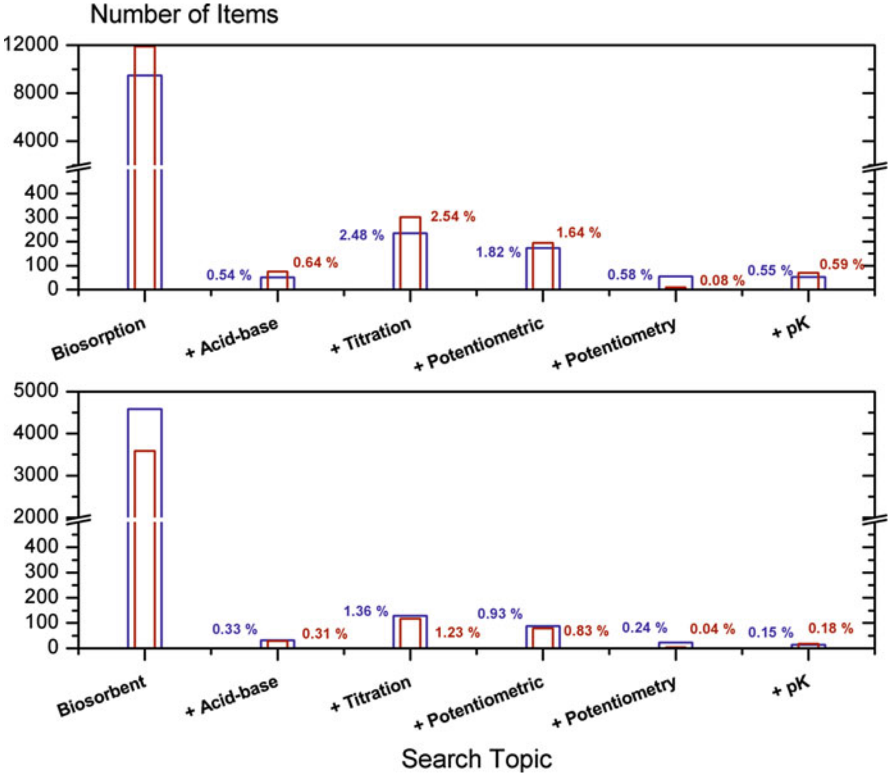

Fig. 3.2 Total bibliography search scores (January 2018) using Scopus (blue bars) and Web of Science (red bars) databases for "biosorption " and "biosorbent", containing any of the key words related to acid-base studies: acid-base, titration, potentiometric, potentiomery or pK. The figure shows that less than 3% of biosorption papers include studies on proton binding

The experimental approach needed for studying proton binding to biosorbents is simple and readily accessible. A potentiometric titration, where the biomass is titrated using a base or acid in a neutral electrolyte solution, constitutes the basics to determine the acidic properties of functional groups in biosorbents. Two crucial parameters can be obtained from potentiometric titrations of biosorbents: the maximum proton-exchange capacity, and the equilibrium dissociation constants of the chemical groups. The former measures the concentration of ionizable functional groups, usually referred to as active binding sites. It is therefore possible to calculate the abundance of potential binding chemical groups involved on pollutant adsorption. As proton binding is predominantly covalent, only other compounds with more covalent character (e.g. heavy metals) will displace the protons from the chemical groups. Therefore, the number of acidic groups obtained from a potentiometric titration is usually considered a potential maximum of binding sites for contaminants, such as metals, endocrine disruptors or dyes. The other key parameter that can be easily obtained from potentiometric titrations, the proton equilibrium dissociation constant, provides the nature of the active chemical sites in the biosorbent. The biosorbents present a high heterogeneity with a range of dissociation constants of their chemical groups (Volesky 2003). This chemical heterogeneity can be also calculated modelling the potentiometric titrations. Nevertheless, the heterogeneity together with the similarity in the equilibrium constant of the chemical groups, make the accurate determination of specific contributions from each binding site challenging (Dewit et al. 1993).

An alternative to the experimental determination of proton binding constants consists in their semi-empirical estimation using Linear Free Energy Relationships (LFER) (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).

In order to ensure that the chemical groups are occupied by protons and not by light metals (Na, K, Mg, Ca), the biosorbents should be fully protonated before performing a potentiometric titration. Light metals are present in natural waters, industrial runoffs and sewage treatment plant effluents. The presence of these elements in solution then 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 review is to characterize the proton binding equilibria, as an extremely important and preliminary step, for a correct interpretation of biosorption results. We first analyze the basics of the acid-base properties of simple substances in saline solutions as starting point for 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 which 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 raised in this review concerning the acid-base studies of biosorbents.

It is worth mentioning that for the sake of simplicity most of the discussions and analysis shown in this review 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 review allows for the description of the biosorption of any pollutant. However, the extrapolation of the results and models considered here to pollutants others than metals should be considered cautiously.

3.2 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 organic compounds is therefore of great importance.

Considering the dissociation of an acid, AH, in aqueous solution (Eq. 3.1) different operational equilibrium constants can be defined:

$$AH \leftrightharpoons A^{-} + H^{+} \tag{3.1}$$

$$K^{T} = \frac{(A^{-})(H^{+})}{(AH)} = \frac{[A^{-}][H^{+}]}{[AH]} \frac{\gamma_{A^{-}}\gamma_{H^{+}}}{\gamma_{AH}} = K^{*} \frac{\gamma_{A^{-}}\gamma_{H^{+}}}{\gamma_{AH}} \tag{3.2}$$

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.

The thermodynamic proton dissociation constant of simple ligands depends on the medium composition, namely on the ionic strength and electrolyte type. As described in Eq. 3.2, this dependency is a function of the activity coefficients of the species involved, which are ions and neutral molecules:

$$K^{T}(P, T, solvent) = K^{*} \cdot Q(\gamma_i) \tag{3.3}$$

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.

Alternatively, taking logarithms and multiplying by RT, Eq. 3.3 can be expressed in terms of the Gibbs free energy (ΔG):

$$\Delta G^{*} = \Delta G^{0} + (\Delta G_{non-elec} + \Delta G_{elec}) = \Delta G_{int} + \Delta G_{elec} \tag{3.4}$$

where the energetic terms associated to the activity coefficients have been split into two parts: electrostatic and non-electrostatic (Sastre De Vicente 1997; Lodeiro et al. 2007) (see Table 3.1 and Sect. 3.2.1); and the term ΔG_{int} includes all the contributions to Gibbs free energy different from the electrostatic ones.

Table 3.1 Main models proposed in bibliography to calculate activity coefficients (γ)

Model	Function	Comments	Type	References
Brönsted	$\log\gamma_{\pm} = -3\alpha\sqrt{c} - 2\beta \cdot c$	Applicable at moderate concentration, c	Empirical	Bronsted (1922a, b)
Limiting Debye-Hückel	$\log\gamma_{\pm} = -A \mid z_{\pm}z_{-} \mid \sqrt{I}$	Applicable at very diluted ionic strength	Theoretical	Debye and Huckel (1923a, b)
Extended Debye-Hückel	$\log\gamma_{\pm} = \frac{-A\lvert z_{+}z_{-}\rvert\sqrt{I}}{1+Ba\sqrt{I}}$	Applicable at diluted ionic strength, size effects	Debye-Hückel based	Debye and Huckel (1923a, b)
Guggenheim	$\ln\gamma_{MX} = -\frac{A'\lvert z_M z_X\rvert\sqrt{I}}{1+\sqrt{I}} + \frac{2v_M}{v_M+v_X}\sum_a \beta_{Ma}m_a + \frac{2v_X}{v_M+v_X}\sum_c \beta_{cX}m_c$	Applicable at moderate ionic strength/ concentration	Debye-Hückel based	Guggenheim (1935)
Hückel	$\log\gamma_{\pm} = \frac{-A\lvert z_{+}z_{-}\rvert\sqrt{I}}{1+Ba\sqrt{I}} + \beta c$	Applicable at moderate concentration/ ionic strength	Debye-Hückel based	Huckel (1925)
MSA	$\log\gamma_i = -\frac{\alpha^2 z_i^2}{4\pi}\frac{\Gamma}{1+\Gamma\sigma_i} - \frac{\alpha^2 z_i\sigma_i}{4(1+\Gamma\sigma_i)}\frac{P_n}{\Delta} + \frac{\pi\alpha^2\sigma_i^3}{16}\left(\frac{1}{1+\Gamma\sigma_i} - \frac{1}{3}\right)\frac{P_n^2}{\Delta^2} - \ln\Delta + \frac{\sigma_i^3 X_0 + 3\sigma_i^2 X_1 + 3\sigma_i X_2}{\Delta} + \frac{3\sigma_i^3 X_1 X_2 + 9/2\sigma_i^2 X_2^2}{\Delta^2} + \frac{3\sigma_i^3 X_2^3}{\Delta^3}$	Inclusion of size and charge effects. Applicable at moderate concentrations/ionic strengths	Statistical mechanics approach based in hard spheres.	Blum (1975)

Pitzer	$\ln\gamma_{M^+} = z_M^2 f^\gamma + 2\sum_a m_a\left[B_{Ma} + \left(\sum mz\right)C_{Ma}\right] + 2\sum_c m_c\theta_{Mc} + + \sum_c\sum_a m_c m_a\left(z_M^2 B'_{ca} + z_M C_{ca} + \psi_{Mca}\right) + \frac{1}{2}\sum_a\sum_{a'} m_a m_{a'}\left(z_M^2\theta'_{aa'} + \psi_{Maa'}\right) + + \frac{z_M^2}{2}\sum_c\sum_{c'} m_c m_{c'}\theta'_{cc'}$	Applicable at very high concentration/ ionic strength	Debye-Hückel based	Pitzer (1973, 1991) and Pitzer and Mayorga (1973)
Sammartano	$\log\gamma_z = \frac{-Az^2\sqrt{I}}{1+B\sqrt{I}} + C_z I + D_z I^{3/2}$	Empirical modification of the extended Debye-Hückel limiting law. Applicable at moderate to high ionic strengths	Debye-Hückel based	Daniele et al. (1997)

The table includes the name and type of model, the equation, information about the range of applicability and relevant bibliography

*For symbol interpretation see references mentioned in the table and references therein

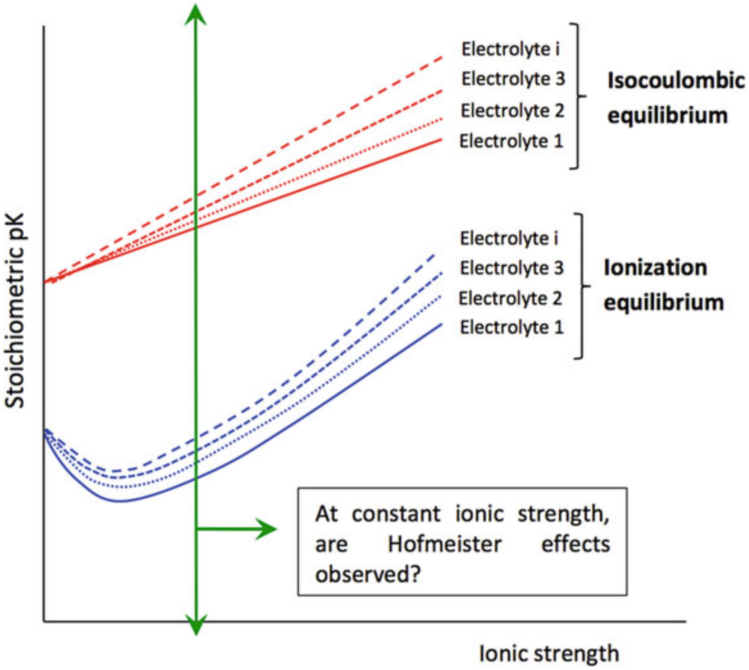

Fig. 3.3 pK* versus ionic strength plot for isocoulombic and ionization acid-base equilibrium. For isocoulombic equilibria, pK* is a linear function of the ionic strength (red lines). On the contrary, the plot shows that for ionization equilibrium curves passes through a minimum (blue lines). Hofmeister effects could be identified at constant 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 (Table 3.1 and references therein), the following equation is obtained at constant P, T and background electrolyte:

$$pK^* = pK^T + f(I, system\ parameters) \tag{3.5}$$

The representation of pK* *versus* ionic strength depends on the electrostatics involved in the acid-base equilibrium. Therefore, in a typical ionization (charge separation) equilibrium (Eq. 3.1), a plot of the pK* dependence on ionic strength commonly passes through a minimum. Nevertheless, the pK* is usually a linear function of the ionic strength when isocoulombic equilibria are involved; this is commonly observed, for example, for amine protonation reactions: $BH^+ \leftrightarrows B + H^+$. An example of these two behaviours can be seen in Fig. 3.3.

The relative proportion of anionic/neutral species, and therefore the balance of the existing interactions for the general proton dissociation equilibrium represented in Eq. 3.1, changes with the pH and ionic strength of a particular solution as follows:

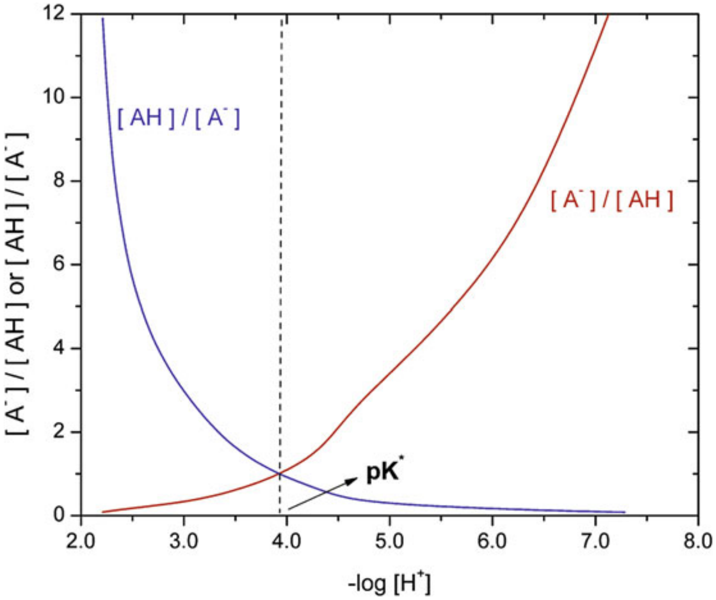

Fig. 3.4 Evolution of the proportion of neutral/anionic (blue line) and anionic/neutral (red line) species with pH. The data represents a potentiometric titration of the brown seaweed *Sargassum muticum* in $NaNO_3$ 0.05 mol·L^{-1} at 25 °C. The intersection of both plots corresponds to the stoichiometric protonation constant, pK*, of the acidic groups present in the seaweed

$$\frac{[A^-]}{[AH]} = \frac{K^*(I)}{[H^+]} = f(I, pH) \tag{3.6}$$

Hence, mainly the pH but also the ionic strength are relevant variables tuning the interactions between solutes present in a specific medium composition (see Fig. 3.4).

3.2.1 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 (Table 3.1). As mentioned in Sect. 3.2 (Eq. 3.4), 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. Although, 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. The ionic strength is therefore considered as a key variable in the study of electrolyte systems, even nearly hundred years after its introduction in chemistry by G. N. Lewis and M. Randall (Sastre De Vicente 1997, 2004). 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 elaborated theory, the Mean Spherical Approximation (MSA), allows the calculation of the activity coefficients term, $Q(\gamma_i)$, including explicitly the ion charge, size and concentration, and the temperature, as parameters in its formulation (Sastre de Vicente and Vilariño 2002). Therefore, the MSA theory allows, for example, studying size effects on chemical equilibria, which is not possible using Specific Interaction Theory expressions.

3.3 Gibbs Free Energy of Proton Binding: Electrostatic and Non-electrostatic Contributions

About 40 years ago, in an already classical work on ionizable surfaces, Healy and White (1978) presented a reaction of dissociation as:

$$AH^{(Q-1)^-} \rightleftarrows A^{Q^-} + H^+ \tag{3.7}$$

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 into non-electrostatic and electrostatic terms in analogy to Eq. 3.4 (Moreno-Castilla 2004):

$$\Delta G_{diss} = \Delta G_{non-elec} + \Delta G_{elec} \tag{3.8}$$

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

$$\Delta G_{diss} = \Delta G^{LW} + \Delta G^{AB} + \Delta G_{elec} \tag{3.9}$$

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. 3.8 and 3.9 allows the identification of the relevant contributions of non-covalent interactions in the $\Delta G_{\text{non-elec}}$ term, also called intrinsic free energy (ΔG_{int}).

The protons are a master variable that control any acid-base system and influence practically all processes in aqueous chemistry (Stumm and Morgan 1996). The pH, as discussed in Sect. 3.2, 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, as previously stated for single acid-base equilibria (Eqs. 3.4 and 3.5), the pH also affects the interactions involved in the different Gibbs free energy contributions (Eq. 3.9). In addition, other parameters such as the ionic strength, and the specific electrolyte nature, influence, as discussed for Eq. 3.4, the energetic terms in Eq. 3.9 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:

$$\Delta G_{ads} = \Delta G_{ads}(pH, I, electrolyte\ nature) \tag{3.10}$$

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 3.10 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 3.9 and 3.10 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. These three key variables are not usually changed simultaneously: for example, a potentiometric titration is usually performed maintaining the nature of the electrolyte and ionic strength constant while changing pH. Afterwards, a series of experiments can be performed at different ionic strengths using the same electrolyte at identical solution temperature. 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.

3.4 Acid-Base Properties in Macromolecular Systems: A Complex Problem

The study of the equilibrium binding shows significant differences between fully characterized simple inorganic ions or organic compounds (e.g. acetic acid), and complex, not well-defined, macromolecules (e.g. humic/fulvic acids, polysaccharides or polyelectrolytes). The study of the acid-base properties of simple organic ligands is straightforward. Nevertheless, the study of ion binding to biosorbents is challenging and requires considering the following singularities (Fig. 3.5):

1. High quantity of binding sites: the number of chemical species involved can be in the order of hundreds to thousands or more. It is convenient then to describe the binding to biosorbents in terms of distribution of species.

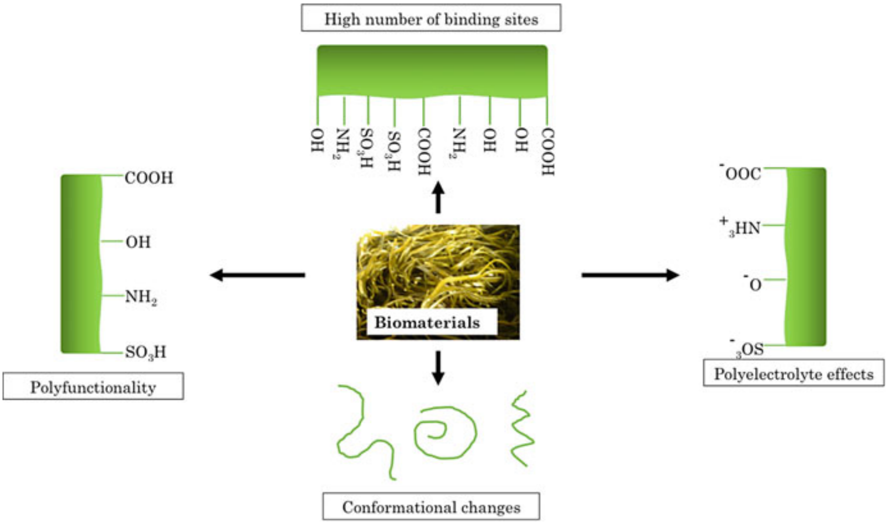

Fig. 3.5 Schematic representation of the main singularities that affect the acid-base and binding properties of biosorbents when compare to simple compounds. That is, presence of high number of binding sites, presence of many different chemical groups (polyfunctionality), conformational changes and polyelectrolyte effects associated with the presence of charged functional groups

2. High polyfunctionality: presence of many different chemical groups such as carboxyl, hydroxyl or amino that can also have different environments, for example linked through aliphatic or aromatic groups. This is also known as chemical heterogeneity.
3. Conformational changes: possible polymer chain reconfigurations depending on solution variables such as pH or ionic strength. The changes in the steric disposition of the binding sites can make them either more or less accessible, and lead to titration hysteresis.
4. Polyelectrolyte effects: the presence of charged functional groups in the biosorbents may constrain further dissociation of binding sites with increasing or decreasing pH values due to a progressive change of electrostatic attractions; as a consequence, the apparent dissociation constant also change.

All those singularities can occur simultaneously and affect to a different extent the acid-base and binding properties of biosorbents, and should then be considered in biosorption studies.

3.5 Classification of Biosorbents Based on Their Functional Groups

Based on the natural sources of biomass in nature, biosorbents are classified broadly into two major categories (Bailey et al. 1999): microscopic biomass that mainly involves microalgae, fungi and bacteria (Sag 2001; Aksu 2005; Vijayaraghavan and Yun 2008a; Wang and Chen 2009); and macroscopic biomass, which comes from a wide variety of sources, among them forestry-based biomass and agricultural residues (Brown et al. 2000; Gardea-Torresdey et al. 2004; Hubbe et al. 2011; Kyzas et al. 2013), marine biomass (e.g. green, red and brown algae) (Plazinski 2013a) or biomass from the seafood processing industry, including crustacean shells and arthropods (Fig. 3.6) (Guibal 2004; Tudor et al. 2006; Morris and Sneddon 2011; Muzzarelli 2011).

If they are classified by majority chemical composition, most of these materials owe their properties to the most abundant biopolymers found in nature, i.e. cellulose, chitin and lignin. Apart from them, alginates, naturally occurring polymers in the cell-wall of brown algae, are showing themselves as one of the most powerful adsorbents of metal ions and organic molecules (Davis et al. 2003). The alginates are chain-forming heteropolysaccharides made up of blocks of mannuronic and guluronic acid. Besides, carrageenans from red and green algae, pectins from fruit, tannins from forestry biomass, fucoidans, xanthates, starch, lipids or proteins are also noteworthy as adsorbents.

A further chemical characterization of the major molecules shows that their interaction with pollutants occurs through certain functional groups that are repeated many times in their polymeric structure. This interaction is responsible for both the adsorption process and the acid-base properties of the biosorbents. It is worth

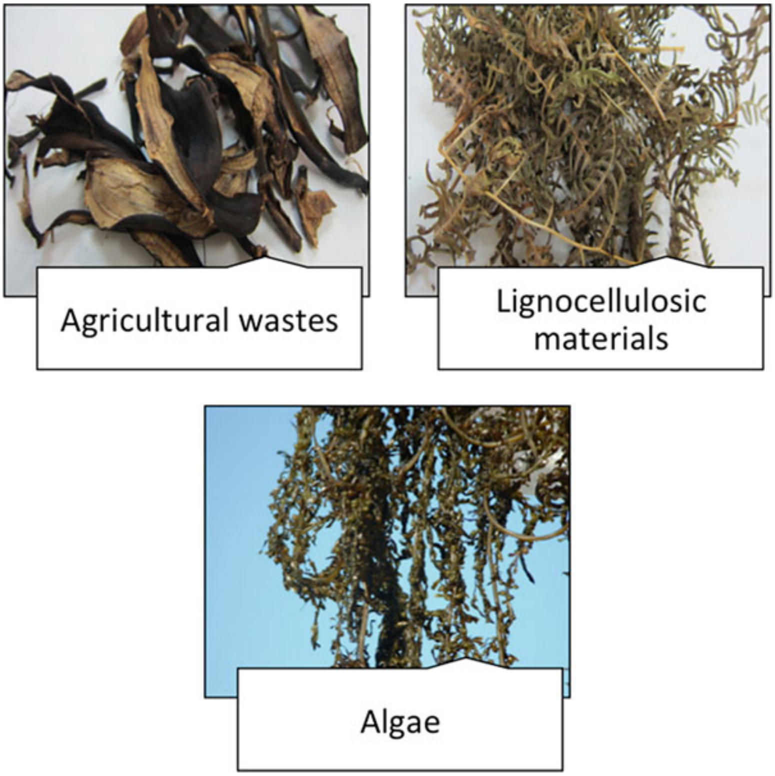

Fig. 3.6 Examples of representative biosorbents obtained from agricultural wastes (banana skin), lignocellulosic materials (fern) and marine biomass (macroalga)

mentioning the carboxyl, hydroxyl, phenolic, amine, amide, phosphonate, acetamide and sulfonate groups, both for their abundance, and for their key role in the acid-base and adsorbent properties of natural biomass.

Large numbers of biosorption studies have been carried out using all sorts of biomass to eliminate different pollutants. However, studies dealing with the determination of the acid-base properties of these materials are scarce, even though they are the basis for interpretation of the main biosorption mechanisms.

The characterization of the acid-base properties is mainly carried out by a potentiometric study of the biomass to determine the type and number of binding sites. These studies allow also equilibrium constants to be obtained and they can be supplemented by other techniques, such as Fourier transform infraRed spectroscopy (FTIR), X-ray absorption near edge structure (XANES), fluorescence spectroscopy, extended X-ray absorption fine structure (EXAFS) or nuclear magnetic resonance (NMR), to identify all the functional groups in the biomass and their role in the adsorption process (Sun and Berg 2003; Joud and Barthés-Labrousse 2015).

3.6 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. 3.8. This division allows simplifying and correctly interpret the proton binding equilibria in biosorption processes under different experimental conditions.

3.6.1 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. As mentioned in Sect. 3.4, 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 Sect. 3.3, 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. 3.8. 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 biding site can be written as (Morel et al. 1993):

$$\Delta G_{elec} = nF\psi_0 = F\psi_0 \tag{3.11}$$

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:

$$K_{elec} = e^{-\frac{\Delta G_{elec}}{RT}} = e^{-\frac{F\psi_0}{RT}} \tag{3.12}$$

Considering the proton dissociation reaction presented in Eq. 3.2, a biosorbent of charge Q will present an apparent dissociation constant (K_{app}) given by:

$$K_{app} = \frac{\left[A^{Q^-}\right]\left[H^+\right]}{\left[AH^{(Q-1)^-}\right]} = \frac{\left(A^{Q^-}\right)\left(H^+\right)}{\left(AH^{(Q-1)^-}\right)}\frac{\gamma_{AH^{(Q-1)^-}}}{\gamma_{A^{Q^-}}\gamma_{H^+}} = K_{int}\frac{\gamma_{AH^{(Q-1)^-}}}{\gamma_{A^{Q^-}}\gamma_{H^+}} \tag{3.13}$$

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 et al. 1993):

$$\ln \gamma_{eff} = \ln \frac{\gamma_{A^{Q-}}}{\gamma_{AH^{(Q-1)^-}}} = -\frac{F\psi_0}{RT} \tag{3.14}$$

The intrinsic dissociation constant can be calculated from:

$$K_{int} = K_{app}\gamma_{H^+}\gamma_{eff} = \frac{\left[A^{Q^-}\right]}{\left[AH^{(Q-1)^-}\right]}(H^+)_0 \tag{3.15}$$

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:

$$(H^+)_0 = [H^+]\gamma_{H^+}e^{-\frac{F\psi_0}{RT}} = (H^+)e^{-\frac{F\psi_0}{RT}} \tag{3.16}$$

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 (Table 3.1) 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 3.16 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 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. 3.7). 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. 3.17), which relates the Laplacian of the electrostatic potential (ψ) to the charge density in the medium (Bartschat et al. 1992).

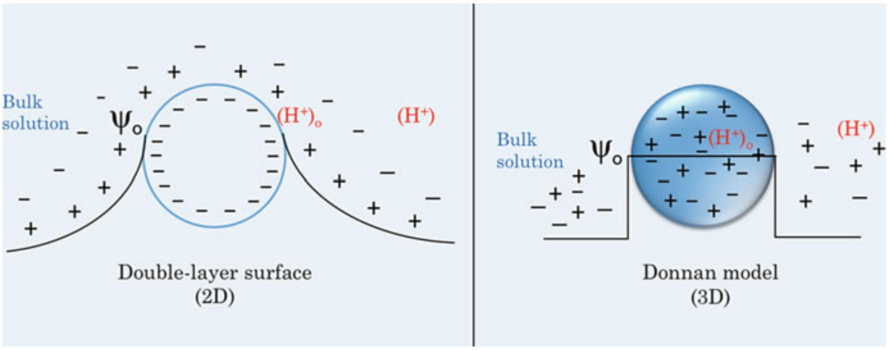

Fig. 3.7 Schematic representation of the double layer surface model (left panel) and Donnan model (right panel). The former considers the active binding sites as a two-dimensional rigid structure. On the contrary, on the later the active sites are represented as a three-dimensional permeable volume

$$\nabla^2\psi = -\frac{1000F}{\varepsilon}\left(\sum_i z_i[X_i]e^{-\frac{F\psi}{RT}} + \rho_0\right) \tag{3.17}$$

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 3.17 is valid either for surface double-layer ($\rho_0 = 0$) or Donnan models, where $\rho_0 \neq 0$.

The Surface Complexation Model (SCM) is one of the most well-known and used surface models. The works of Borrok et al. (2005) and Goldberg and Criscenti (2008) constitute a good review for this matter. Table 3.2 shows several examples where the SCM model and the alternative Donnan approach were used in biosorption studies. It is worth mentioning that most of the references shown in Table 3.2 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.

The application of the finite difference method allows the more general non-linear Poisson-Boltzmann equation to be solved, with important implications on diverse biological and chemical phenomena (Honig and Nicholls 1995).

The macroscopic Donnan model can be considered as a special case of the microscopic Poisson-Boltzmann theory (Dahnert and Huster 1999). In fact, both models represent essentially the same electrostatic and osmotic phenomena. Nevertheless, the Donnan model is simpler and does not require a solution to the Poisson–Boltzmann equation; the Donnan model relates the electrostatic effects to the difference between the bulk and local concentrations multiplied by the volume of the binding sites.

Table 3.2 Compilation of potentiometric experiments for different biosorbents 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	References
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. (2003, 2004a)
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. (2004, 2005a, b, 2006a)
Brown algae	No	No	No	No	No info	3–10	0.001	NaCl	Fourest and Volesky (1997)
Brown algae	No	No	No	Discrete (one site)	No info	2.5–4.5	0.1	$NaNO_3$	Seki and Suzuki (1998)
S. Polycystum (brown alga)	No	Davies equation	No	Discrete (three sites)	No info	2–10.5	0.1 and 1	$LiNO_3$	Yun and Volesky (2003) and Yun (2004)
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)
Alginate	Donnan	No	Yes	NICA (L-F) (one site)	Buffers pH 4, 7 and 9	3–8	0.005–0.3	KNO_3	Lamelas et al. (2005)
U. pinnatifida (green alga)	Gouy-chapman	No	No	Discrete (two sites)	No info	2.5–11	0.0001–1	NaCl	Kim et al. (1998)
P. subcapitata (green alga)	No	No	No	Discrete (four sites)	No info	3–10	0.1	$NaClO_4$	Kaulbach et al. (2005)
C. vulgaris (green alga)	No	No	No	Discrete (four sites)-continuous sips (L-F)	No info	2–12	0.1	$NaNO_3$	Pagnanelli et al. (2013)
Vaucheria sp. (green alga)	No	No	No	No	No info	3–11	Not fixed	Deionised water	Crist et al. (1981)
Ulva lactuca (green alga)	No	Extended Debye-Hückel	No	Discrete (three sites)	Proton concentration	2–10	0.01–5	NaCl	Schijf and Ebling (2010)
G. sesquipedale (red alga)	No	No	No	Discrete (two sites)-continuous sips (L-F)	Proton concentration	3.5–10.5	0.005–0.1	$NaNO_3$	Vilar et al. (2009)
Phyllophora crispa (red alga)	No	No	No	Discrete (three sites)/Katchalsky	No info	3–10	0.01	NaCl	Meichik et al. (2011)
Chlorella miniata (microalga)	No	No	No	Discrete (three sites)	No info	3.5–10.5	Not fixed	Deionised water	Han et al. (2006)
Olive Pomace	No	Davies equation	No	Discrete (two sites) -continuous L-sips	No info	2–10	Not fixed 0.07–0.09	Deionised water	Pagnanelli et al. (2005b)
Olive Pomace	No	Davies equation	No	Discrete (one-two sites) -continuous L-sips- NICA (L-F)	Buffers pH 4 and 7	2–	Not fixed	Deionised water	Pagnanelli et al. (2005a)

(continued)

Table 3.2 (continued)

Biosorbent	Electrostatic proton binding model	Specific Interaction Model	Master curve approach	Chemical proton binding model	Electrode calibration	pH range	Ionic strength mol/L	Electrolyte	References
Olive Pomace	No	No	No	Continuous L-sips	No info	2.5–9.5/11.5	Not fixed	Deionised water	Pagnanelli et al. (2008)
Olive Pomace	No	No	No	Discrete (two sites) -continuous L-sips	No info	2–12	Not fixed	Deionised water	Pagnanelli et al. (2003)
Olive Pomace	No	No	No	Discrete (two sites) -continuous sips	No info	2–9.5/10	Not fixed	Deionised water	Martín-Lara et al. (2008)
Olive oil production waste	No	No	No	Discrete (three sites)	No info	3–11	Not fixed	Deionised water	Calero et al. (2010)
Sugar beet pulp	Diffuse layer	No info	No	Discrete (three sites)	No info	3–11	0.001–0.1	$NaNO_3$	Reddad et al. (2002)
Wheat bran substrate	Donnan	No	Yes	NICA (L-F) (two sites)	Proton concentration	3.5–8	0.04–1	$NaNO_3$	Bouanda et al. (2002)
Wheat bran substrate	Diffuse layer	Davies equation	No	Discrete (two sites)	Buffers pH 4, 7 and 10	2.5–11	0.01–0.1	$NaNO_3$	Ravat et al. (2000)
Citrus peels	No	No	No	Continuous pK spectrum (FOCUS), (4 sites)	No info	2.5–11	Not fixed	Nano-pure water	Schiewer and Patil (2008a)
Orange peel/bracken fern	No	No	No	Discrete (two – Three sites)	Proton concentration	3–11.5	0.05	$NaNO_3$	Lodeiro et al. (2008)
Banana skin	No	No	No	Discrete (two sites)	Proton concentration	3.5–11	0.1	KNO_3	Lopez-Garcia et al. (2013)
Bracken fern	No	No	No	Katchalsky	Proton concentration	No info	0.05	KNO_3	Barriada et al. (2009)
Festuca rubra (grass)	No	No	No	Discrete (three sites)	Buffers pH 2, 4, 7 and 10	2.2–9.7	0.1	$NaClO_4$	Ginn et al. (2008)

Cumin	No	No	No	Discrete (two sites)	No info	2–10	0.1	$NaNO_3$	Komy (2004)
Bamboo sawdust	Donnan	No	Yes	NICA (L-F) (two sites)	No info	3.5–10.5	0.01, 0.1, 1	KNO_3	Zhao et al. (2015)
Peat	Donnan	No	No	NICA (L-F) (two sites)	Proton concentration	3.5–10	0.1–0.3	KNO_3	Lopez et al. (2011)
Modified peat	No	No	No	Discrete (four sites)	No info	4–11	0.01	$NaNO_3$	Randelovic et al. (2016)
C. glutamicum (bacteria)	No	No	No	Discrete (three sites)	No info	3–11	Not fixed	Water	Vijayaraghavan and Yun (2008b)
Bacillus subtilis (bacteria)	No	Davies equation	No	Discrete (five sites)	Buffers pH 4, 7 and 10	4–10	0.025 and 0.1	$NaNO_3$	Cox et al. (1999)
Bacillus subtilis (bacteria)	Constant capacitance	No	No	Discrete (three sites)	Proton concentration	2.1–9.7	0.1	NaCl	Leone et al. (2007)
Bacillus subtilis (bacteria)	Constant capacitance	No	No	Discrete (three sites)	No info	3.5–10.5	0.1 and 0.3	$NaNO_3$	Fein et al. (1997)
Bacillus subtilis (bacteria)	Constant capacitance	No	No	Discrete (two-four sites)-continuous L-F	Proton concentration/ buffers	2–10	0.01–0.3	$NaClO_4$	Fein et al. (2005)
Bacillus subtilis (bacteria)	Donnan	Davies equation	No	No	No info	2.4–9	0.001, 0.01 and 0.1	KNO_3	Yee et al. (2004)
A. flavithermus (bacteria)	Donnan	Davies equation	No	Discrete (three sites)	No info	3.5/4–9/10	0.001, 0.01 and 0.1	$NaNO_3$	Burnett et al. (2006)
A. flawithermus (bacteria)	Donnan	No	No	Discrete (two sites)	No info	3–10	0.01/0.5	$NaNO_3$/ NaCl	Heinrich et al. (2007)
Pseudomonas sp. (bacteria)	Diffuse layer/triple layer	Davies equation	No	Discrete (four sites)	No info	2.5–9.7	0.01, 0.1 and 0.5	$NaClO_4$	Borrok and Fein (2005)

(continued)

Table 3.2 (continued)

Biosorbent	Electrostatic proton binding model	Specific Interaction Model	Master curve approach	Chemical proton binding model	Electrode calibration	pH range	Ionic strength mol/L	Electrolyte	References
P. aeruginosa (bacteria)	No	No	No	Discrete (three sites)	No info	3–10	0.1	$NaNO_3$	Komy et al. (2006)
P. pseudo-alcaligenes (bacteria)	Constant capacitance	No	No	Discrete (one-three sites)	No info	2.5–10.5	0.01, 0.1 and 0.5	$NaNO_3$	Liu et al. (2013)
A. manzaensis (bacteria)	Donnan	No	No	Discrete (three sites)	No info	2–10	0.001, 0.01 and 0.1	$NaNO_3$	He et al. (2013)
S. putrefaciens (bacteria)	Constant capacitance	No	No	Discrete (three sites)	No info	4.2–9.5	0.1	NaCl	Haas (2004)
S. natans (bacteria)	Donnan	No	No	Discrete (two sites) -continuous L-sips	No info	3–10	0.1	$NaNO_3$	Pagnanelli et al. (2004)
Bacteria sp.	Constant capacitance	No	No	Discrete (five sites)	No info	3–11	0.01	$NaNO_3$	Ngwenya et al. (2009)
Bacteria sp.	No	No	No	Discrete (four sites)	No info	3–10	0.1	$NaClO_4$	Kenney and Fein (2011)
Bacteria sp.	Donnan	Yes (no info)	Yes	Continuous pK spectrum (FOCUS), (4 sites)	Buffers pH 4, 7 and 10	3–10	0.01–0.5	KNO_3	Martinez et al. (2002)
Bacteria sp.	No	No	No	Discrete (four sites)	No info	2.7–9.5	0.1	$NaClO_4$	Mishra et al. (2010)
Bacteria sp.	Donnan	No	Yes	Continuous L-F	Proton concentration	3–10.5	0.01, 0.1 and 1	$NaNO_3$	Plette et al. (1995)
Bacteria sp.	No	No	No	Discrete (three sites)	No info	4–10	0.001	NaCl	Guine et al. (2006)

Gloeocapsa sp. cyanobacteria	No	No	No	Discrete (three sites)	No info	3–11	0.01–1	$NaNO_3$/ NaCl	Pokrovsky et al. (2008)
Cyanobacteria	No	No	No	Discrete (three sites)	No info	0.5–11.5	0.1	$NaNO_3$	Gagrai et al. (2013)
Pico-cyanobacteria strains	No	No	No	Discrete (two-three sites)	Buffers pH 4, 7 and 10	2.9–10	0.01	$NaNO_3$	Dittrich and Sibler (2005)
Aspergillus niger (fungi)	No info	No	No	Discrete (two sites)	No info	3–11	Not fixed	Distil water	Mukhopadhyay (2008)
Saccharomyces Cerevisiae (fungi)	Constant capacitance	No	No	Discrete (four sites)	No info	3–9.7	0.001, 0.1 and 0.3	$NaClO_4$	Naeem et al. (2006)
S. cerevisiae (yeast)	No	No	No	Discrete (three sites)	No info	2–10	0.1 and 1	$NaNO_3$	Di Caprio et al. (2014)
Archeon	Yes (no info)	No	No	Discrete (three sites)	No info	3.5–9.5	0.01	$NaNO_3$	Daughney et al. (2010)
Diatoms	Constant capacitance	No	No	Discrete (three sites)	No info	2.3–11.5	0.001–1	NaCl/ $NaNO_3$	Gelabert et al. (2004)
Phytoplankton sp.	No	No	No	Discrete (three sites)	No info	2–12	0.7	NaCl	Gonzalez-Davila et al. (2000)

On this model the electrostatic potential at the active binding site is given by Wonders et al. (1997):

$$\psi_0 = arcsinh\left(\frac{-Q/V_D}{2I}\right) \tag{3.18}$$

where V_D is the active Donnan volume. Equation 3.18 is obtained considering a homogeneously distributed charge within a finite volume, assuming overall electroneutrality and that the active volume dimension is much larger than the Debye length. A more general solution of the Poisson-Boltzmann equation has been proposed by Ohshima and Kondo (1991).

On the contrary, theoretical models based on electrostatics, such as double-layer surface models, require the resolution of the Poisson–Boltzmann equation. This equation can be more or less easy to solve depending on the particular geometry and charge distribution considered for the system. For example, the SCM accounts for the electrostatic effects by a term including the potential at the plane of the adsorption, which is considered as an infinitive flat surface. In this case, the electrostatic potential at the active binding site is given by (Lyklema 1995):

$$\psi_0 = 2arcsinh\left(\frac{-\overline{\sigma}}{\sqrt{I}}\right) \tag{3.19}$$

$$\overline{\sigma} = \frac{\sigma}{\sqrt{8 \times 10^3 \varepsilon\varepsilon_0 RT}} \tag{3.20}$$

where $\sigma = -QF/A$, is the charge density and A the specific surface area.

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 (Schiewer and Volesky 1997a, b; Schiewer 1999; Schiewer and Wong 2000; Rey-Castro et al. 2003; Pagnanelli et al. 2004; Rey-Castro et al. 2004b), 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 biosorbent 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 (Fein et al. 1997; Grenthe 2002; Haas 2004; Rey-Castro et al. 2004a; Borrok and Fein 2005; Fein et al. 2005; Leone et al. 2007; Ngwenya et al. 2009; Liu et al. 2013). 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 (Rey-Castro et al. 2004a, b; De Stefano et al. 2005). In fact, Donnan models have been successfully applied to bacterial biomass (Plette et al. 1995; Martinez et al. 2002; Pagnanelli et al. 2004; Yee et al. 2004; Burnett et al. 2006; Heinrich et al. 2007; He et al. 2013), and double layer models to agriculture derivatives (Ravat et al. 2000; Reddad et al. 2002) or algae biomass (Kim et al. 1998).

3.6.2 Validation of the Accuracy of Electrostatic Models

The electroneutrality condition for solutions states that the addition of positive and negative electric charges, considering the solution as a whole, must be zero. The electroneutrality condition is not a fundamental law of nature, but despite its ambiguous definition is very useful when studying chemical processes in solution. Moreover, it constitutes an excellent approximation to reality on the basis of the Poisson's equation of electrostatics (Sastre and Santaballa 1989).

The master curve approach, for example, is built on the electroneutrality condition. This approach consists on performing potentiometric titrations against a simple ion, usually the proton, in an electrolyte solution at different ionic strengths (see Fig. 3.8).

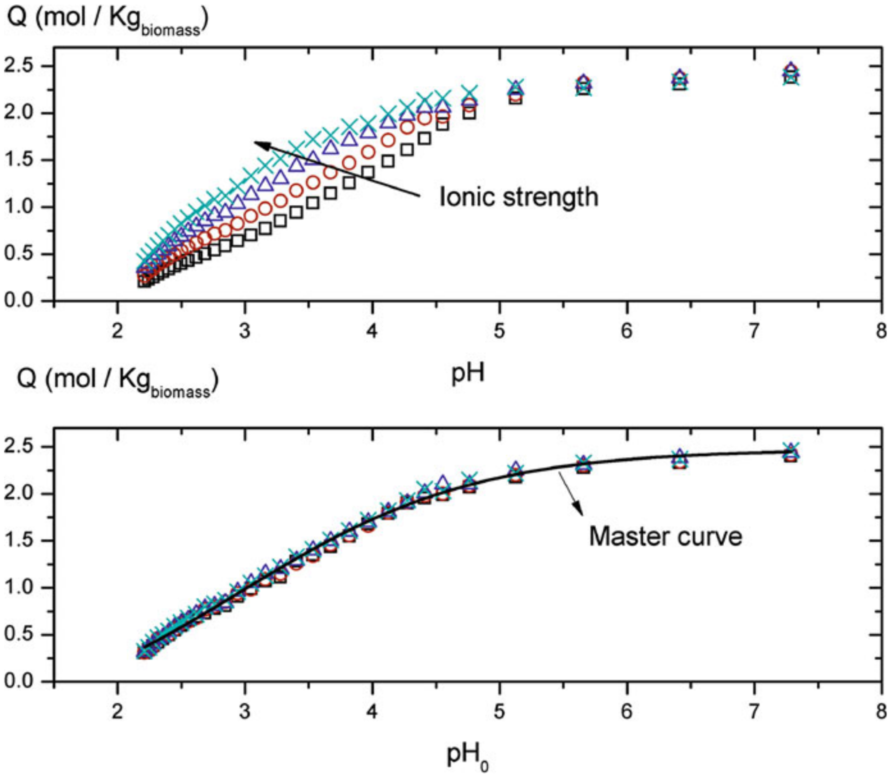

Fig. 3.8 Simulated data of charge versus pH curves (top graph) and calculated master curve (bottom graph) in a specific electrolyte solution. The master curve approach is built on the electroneutrality condition, so the proton binding data can be transformed into data of net charge. If the electrostatic model is correct, the dependence of the binding on ionic strength vanish; therefore, the corrected binding curve merge into the master curve that is independent of the ionic strength as can be observed in the bottom graph

The main goal is to obtain a validation test of the electrostatic model used to describe the charged biosorbent. 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 Sect. 3.9 for details).

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

$$Net\ charge = function(pH, I) = function_b(pH_0) \tag{3.21}$$

where pH_0 ($-\log\ [H^+]_0\gamma_{H+}$), the pH at the local binding site, can be obtained from Eq. 3.16.

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 curve will merge into the so-called master curve that is independent of the ionic strength (Eq. 3.21).

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

3.6.3 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). At the end of the nineteenth-century, Hofmeister investigated the concentration requirements of distinct salts in precipitating egg white lecithin and found the following standard sequence for a fixed cation: $SO_4^{2-} > OH^- > F^- > Cl^- > Br^- > NO_3^- > I^- > SCN^- > ClO_4^-$, and for a fixed anion: $NH_4^+ > K^+ > Na^+ > Cs^+ > Li^+ > Rb^+ > Mg^{2+} > Ca^{2+} > Ba^{2+}$.

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. 3.9 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, and unquantifiable terms such as hydration, hydrophilic, hydrophobic, π-cation interactions, hydrogen bonding, soft-hard ions, chaotropic, cosmotropic, etc. have been used in the derivation of these dispersion forces. However, the use of some simple empirical rules, such as the "law of matching water affinities" (Collins 2004; Collins et al. 2007; Vlachy et al. 2009), allows for the description of an important number of the above mentioned properties.

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):

$$c_{\pm} = ce^{\pm\frac{(z_i e\psi + U_{\pm})}{kT}} \tag{3.22}$$

Therefore, the Eq. 3.16 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 (Para and Warszynski 2007; Nelson and Schwartz 2013) 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.

3.6.4 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. 3.1 but considering AH as a whole (not only a specific acid site). The apparent conditional dissociation constant (K_{app}) can be written then as:

$$pK_{app} = pH - log\frac{\alpha}{1-\alpha} \tag{3.23}$$

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

$$\alpha = \frac{[A^-]}{[A^-]+[AH]} \tag{3.24}$$

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. 3.2), 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. 3.25) 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:

$$pH = pK_m + n\ log\frac{\alpha}{1-\alpha} \tag{3.25}$$

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:

$$pK_{app} = pK_m - (n-1)\ log\frac{\alpha}{1-\alpha} \tag{3.26}$$

$$pK_{app} = pK_m - \left(\frac{n-1}{n}\right) pH \tag{3.27}$$

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 (Fig. 3.9).

The best description of the binding properties of biosorbents has been provided therefore, when the model explicitly includes both, heterogeneity and

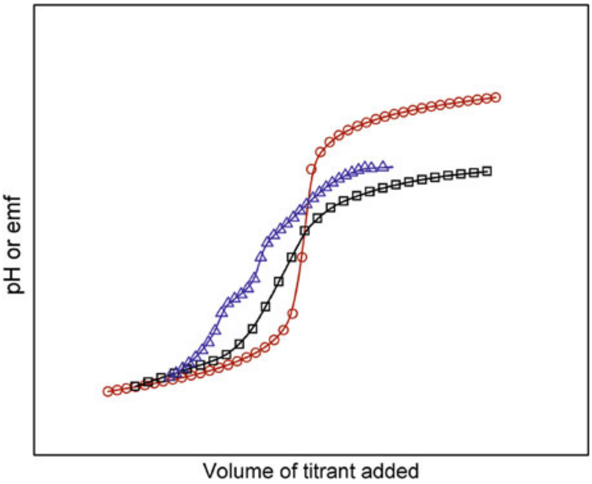

Fig. 3.9 Experimental titration curves for the simple organic compound tris(hydroxymethyl) aminomethane, Tris (red), the macroalga *Sargassum muticum* (black) and the lignocellolosic material *Pteridium aquilinum*, fern (blue). The graph evidences the stepper character and simplicity of the Tris titration curve compared to the obtained for a biosorbent with multifunctional binding sites

polyelectrolytic effects (despite conformational changes, not explicitly reflected). Therefore, reorganising Eq. 3.16 and substituting in Eq. 3.23 provides with an expression for the solution pH ($-\log [H^+]\gamma_{H+}$) or pK_{app}:

$$pH = pK_{int} + log\left(\frac{\alpha}{1-\alpha}\right) - \frac{1}{\ln 10 \frac{e\psi_0}{kT}} \tag{3.28}$$

$$pK_{app} = pK_{int} - \frac{1}{\ln 10 \frac{e\psi_0}{kT}} \tag{3.29}$$

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 refer 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 linear increase 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.

3.6.5 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:

$$\theta = 1 - \alpha = \frac{[AH]}{[A_{tot}]} = \frac{[AH]}{[A^-] + [AH]} \tag{3.30}$$

The plot of θ *vs* $[H^+]$ is called the biding 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:

$$\theta([H^+]) = \int_0^\infty p(K) f([H^+], K) dK \tag{3.31}$$

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:

$$f_{CA}(\log K = -\log[H^+]) = \frac{d\theta}{d\log[H^+]} \tag{3.32}$$

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 (Lodeiro et al. 2006b; Herrero et al. 2011; 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 (Rudzinski and Plazinski 2010; Plazinski 2013b). 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 been also studied (Plazinski and Rudzinski 2009, 2011).

It should finally be mentioned that in addition to the NICA-Donnan model, there are other models commonly used for studying the metal-natural organic matter (NOM) interactions; those are the Windermere humic aqueous model (WHAM), including three different versions (V, VI and VII) (Tipping 2002; Groenenberg and Lofts 2014), and the Stockholm humic model (Gustafsson 2001). The WHAM model is a discrete site model used to describe the binding of protons and metal cations to humic substances. This model has been mainly applied to speciation studies in freshwaters; although both WHAM and NICA-Donnan models, have been applied for the first time at ionic strengths greater than 1 mol kg^{-1} (Marsac et al. 2017). The WHAM models can provide, in general, similar results to the ones obtained using the NICA-Donnan continuous distribution site approach. Nevertheless, only the later model is applied to adsorption/biosorption studies. However, both models have been used for proton binding determinations, and several comparisons between them can be found in the literature (Christensen et al. 1998; Tipping 2002; Dudal and Gerard 2004; Merdy et al. 2006).

3.7 Nature, Abundance and Strength of Functional Sites in Biosorbents

Despite the wide variety of biopolymers and, therefore, of functional groups, almost all potentiometric studies practically agree that the acid-base properties of different types of natural biomass are mainly due to the contribution of the surface carboxyl and phenolic groups.

Several authors have studied the acid-base properties of a lignocellulosic substrate extracted from wheat bran. Ravat et al. (2000) characterized the solid by IR and ^{13}C-NMR and studied the proton binding by potentiometric titrations. These authors found that the substrate can be represented by two acid groups, a carboxylic and a phenolic one, at a concentration of 0.08 $mmol{\cdot}g^{-1}$ and 0.28 $mmol{\cdot}g^{-1}$, respectively. By using a discrete two-pK model combined with an electrostatic double-layer model, the surface acidity constants were found to be 3.37 and 8.34, which was attributed to the pK of carboxylic and phenolic groups, respectively. Bouanda et al. (2002) also studied a lignocellulosic substrate obtained from wheat bran. The potentiometric and conductimetric techniques were both used to quantify the number of acid functional groups and to determine the proton-binding constants with the NICA-Donnan model. The number of acid groups found was 0.54 $mmol{\cdot}g^{-1}$ for the carboxylic groups and 0.31 $mmol{\cdot}g^{-1}$, for the phenolic groups, whereas the acidity constants were 5.51 and 7.22, respectively. Bouanda's results are somewhat different from those of Ravat et al. That might be due to the different proportion of fatty acids on the substrates studied, because of the different physicochemical treatment used in the extraction, and the different models used to analyse the data. The NICA-Donnan model takes into account both the swelling behaviour and the heterogeneity of the lignocellulosic substrate. The NICA-Donnan model was also employed by Li and Englezos to describe the proton binding to lignocellulosic substrate extracted from wheat bran (Li and Englezos 2005). The authors reported 0.68 mmol·g^{-1} of carboxylic groups and 0.23 mmol·g^{-1} of phenolic groups, with protonation constants values of 6.30 and 7.61, respectively. Fern is another lignocellulosic substrate that has been often employed in biosorption studies, given its abundance in nature. Barriada et al. (2009) studied the acid-base properties and heavy metal adsorption capacity of bracken fern (*Pteridium aquilinum*). The analysis of acid-base titration data by using the Katchalsky model allowed the authors to obtain a total number of acid groups of 0.432 mmol·g^{-1}and a pK value of 4.37. Lodeiro et al. (2008) also investigated fern biomass; a total number of acid groups of 0.67 mmol·g^{-1} and a pK value of 4.24 were obtained. The results from both studies agree with the contribution of the carboxylate groups for the lignocellulosic substrates previously described. However, Lodeiro et al. proposed a model with two and three functional groups to take into account the heterogeneity of the material. Both models provided similar results. When two functional groups were considered, the results agreed with those found for any lignocellulosic material.

Many authors have also investigated the acid-base properties of different agricultural wastes. Reddad et al. (2002) studied the sugar beet pulp, that consists essentially of polysaccharides (72% of the dry matter); glucose, arabinose and galacturonic acid are the main components, all of them in similar proportions and close to 20%. A discrete model with three surface functional groups combined with a diffuse double layer model was proposed. The contribution of the carboxylic groups was split into two, strong and weak contributions, and the third functional group corresponds to the phenols. The authors reported 0.246 mmol·g^{-1} of strong carboxyl groups, 0.220 mmol·g^{-1} of weak carboxyl groups and 0.109 mmol·g^{-1} of phenolic groups, and the corresponding protonation constants were 3.43, 6.05 and 7.89, respectively.

Fruit wastes have also been studied as promising biosorbents. Peels derived from several fruits consist primarily of cellulosic materials rich in pectin, a polysaccharide based on poly-galacturonic acid. Schiewer and Patil (2008b) studied the behaviour of citrus peels. The use of a continuous model revealed four acidic groups with pK values of 3.8, 6.4, 8.4 and 10.7 and a total site quantity of 1.14 mmol·g^{-1}. Lodeiro et al. (2008) studied acid-base properties of orange peels. The use of a discrete model with two types of binding sites positions resulted in the pK values of 4.00 and 10.35 and the concentrations of 0.49 mmol·g^{-1} and 1.43 mmol·g^{-1} for each functional group. López-García et al. (2013) obtained similar results when banana skin was studied.

Pagnanelli et al. (2003, 2005a, 2008) have carried out an extensive work to study the acid-base and the complexation properties of a very abundant waste from olive oil production plants, olive pomace. This solid residue consists of fibre (as cellulose), lignin and uronic acids along with oily wastes and polyphenolic compounds. The analysis of the native material, as well as its different fractions and chemical modifications, allows the carboxyl and phenolic groups to be identified as the main active sites responsible for the acid-base behaviour and the metal complexation. From the native material, the authors reported concentrations of 0.17 mmol·g^{-1} of carboxyl groups and 0.49 mmol·g^{-1} of phenolic groups with pK values of 4.0 and 8.9, respectively (Pagnanelli et al. 2008).

Many different types of biomass have been investigated, but marine biomass, particularly brown algae, is probably the most widely studied adsorbent substrate. Brown algae have been found to be very effective for metal binding due to their high content of alginic acid in the cell wall, which may comprise between 14 and 40% of the dry weight (Percival and McDowell 1967; Davis et al. 2003). Alginic acid is a natural polysaccharide containing β-D_mannuronic and α-L guluronic acid residues arranged in a non-regular linear chain. Its acid-base properties have been studied by a number of authors. Haug (Haug 1961) studied alginates from different sources, mainly Laminaria algae, and he found that the proportion of the two uronic residues in the alginate determine the acid-base/physical properties and reactivity of the polysaccharide. The pK values of 3.38 and 3.65 were found for mannuronic and guluronic acid, respectively. De Stefano et al. (2005) investigated the acid-base behaviour of sodium alginate by potentiometric and calorimetric titration measurements. The dependence on the ionic strength of the protonation constants were analysed by a modified specific interaction theory (SIT) model. Lin and Marinsky (1993) studied the saline effect on the basis of a Gibbs-Donnan based approach. Rey-Castro et al. (2004b) also investigated this effect based on the Gibbs-Donnan and the specific-ion interaction theories.

The interaction of protons and metals with algae was first investigated by Crist et al. in the 1980s (Crist et al. 1981, 1988). Their studies were focussed on different types of green algae, macroscopic freshwater ones, such as *Vaucheria*, or filamentous ones, such as *Spyrogyra* or *Oedogonium* (Crist et al. 1988). These authors found that adsorption occurs due to the electrostatic interaction of the protons and the metal ions with the carboxylic groups from the cell wall pectin of the green algae.

Volesky and co-workers have been the largest contributors to the study of adsorption processes by use of marine biomass. Their research covers the biosorption of pollutant metals, precious metals, radionuclides, anions, the adsorption mechanisms, continuous processes, modelling tools and also the study of the acid-base properties of algae.

Fourest and Volesky (1996) investigated the two potential ligands present in brown algae: carboxyl and sulfonate groups. The brown seaweed of *Sargassum fluitans* was firstly studied. Simultaneous potentiometric and conductimetric titrations, together with chemical analysis, gave information concerning the amount of strong and weak acidic functional groups in the biomass, 0.25 mmol·g^{-1} for the sulfonate groups from fucoidans and 2.00 mmol·g^{-1} for the carboxylic groups from alginates, respectively; a third contribution due to polyphenols was also found. Later on, the study was extended to four different brown algae *Sargassum fluitans, Ascophyllum nodosum, Fucus vesiculosus*, and *Laminaria japonica,* that were characterized by using potentiometric titrations, ^{13}C-NMR, chemical analysis, and viscosity measurements (Fourest and Volesky 1997).

Schiewer and Volesky (1997b) studied the brown alga *Sargassum*. The Donnan model, that had been previously applied to humic and fulvic acids, was used for interpretation of potentiometric data at different ionic strengths. Furthermore, these authors also studied the swelling of *Sargassum* particles, which was explained by a simple linear relationship between swelling and pH.

Schiewer and Wong (2000) studied the green alga *Ulva Fascia* and the brown algae *Sargassum hemiphyllum*, *Petalonia fascia*, and *Colpomenia sinuosa*. From potentiometric measurements, the total amount of binding sites was determined. The number of carboxylic groups were found to decrease in the order *Petalonia* (2.9 $\text{mmol}\cdot\text{g}^{-1}$) > *Sargassum* (2.6 $\text{mmol}\cdot\text{g}^{-1}$) > *Colpomenia* (1.5 $\text{mmol}\cdot\text{g}^{-1}$) > *Ulva* (1.1 $\text{mmol}\cdot\text{g}^{-1}$). The titration curves for all algae showed a marked effect of ionic strength and the Donnan model was successfully used to account for this effect. The same pK_{app} value 3.0 can be used for all algae.

Sastre de Vicente and co-workers have also contributed significantly to studying the adsorption properties of marine algae, and their acid-base behaviour in particular.

Rey-Castro et al. (2003) carried out an extensive study on the acid-base properties of three brown algae: *Sargassum muticum*, *Cystoseira baccata* and *Saccorhiza polyschides*. The proton binding equilibria of the three seeweeds was studied potentiometrically and the effect of pH, ionic strength and composition of the medium was investigated. The Donnan model combined with the master curve approach was used to interpret the influence of the ionic strength. Different empirical expressions that describe the swelling behaviour of the sorbents were tested. The results showed very little influence of the type of electrolyte. The dependence of proton binding capacity on the ionic strength was very similar for the three algae. The maximum proton binding capacities obtained ranged between 2.4 and 2.9 $\text{mmol}\cdot\text{g}^{-1}$ and the average intrinsic proton affinity constants ranged between 3.1 and 3.3. These data were then re-analysed to compare two opposite and ideal electrostatic models, the Donnan model and the so-called surface charge model (Rey-Castro et al. 2004a). The Donnan model assumes the interphase to behave as a permeable three-dimensional gel that shows an effective Donnan volume, whereas the surface charge model describes the system as a non-permeable two-dimensional surface with a specific surface area as main feature. Both models seemed to be almost equivalent, although the Donnan model provided slightly better results and a simpler way to account for the effect of activity coefficients and the non-specific binding.

Further studies on *Sargassum muticum* have been considered of great interest, as this alga is an invasive species in European waters. Different approximations, e.g. NICA model or Katchalsky model (Katchalsky et al. 1954) were applied to analyse the acid-base properties (Lodeiro et al. 2004, 2005b). Katchalsky model was also applied to study the brown algae *Cystoseira baccata* (Lodeiro et al. 2006a), *Bifurcaria bifurcata*, *Saccorhiza polyschides*, *Ascophyllum nodosum*, *Laminaria ochroleuca* and *Pelvetia caniculata* (Lodeiro et al. 2005a). Similar results were found for all the brown algae. The total number of weak acid groups was large and in the range from 2.43 to 3.33 $\text{mmol}\cdot\text{g}^{-1}$. All the pK_{app} values were found to be around 3.5, which can be identified with the alginic acid, specifically with the mannuronic and guluronic acids.

3.8 The Role of the Acid-Base Properties of Biosorbents on Metals Removal

This chapter is focused on some selected examples where the interactions of biomass with metals are described. The main reasons for the specific selection of metal binding biosorption studies, and not others dealing with the interactions of organic pollutants (e.g. dyes, phenols or endocrine disruptors) are explained below.

As previously mentioned, the main goal of this review is to study the interactions of protons with biosorbents, i.e. their acid-base properties, both from a theoretical and experimental point of view. These acid-base properties are the main factor responsible for the interactions of either metals or organic substances with the surface of the biosorbents. The great majority of c.a. 16,000 papers (SciFinder database) related to biosorption studies investigated metal-biomass interactions, with a minority of studies dedicated to the investigation of organic pollutants. Moreover, the interpretation of the interactions of organic substances with biosorbents is more challenging than the interpretation of the respective metal interactions. As in the case of metals, the presence of ionized organic substances in solution results in electrostatic effects. These charge-related effects are influenced by pH, ionic strength, and electrolyte type. Moreover, the organic substances, e.g. pesticides, dyes, phenols, nitro compounds or endocrine disrupting chemicals, present a great structural variety. This chemical diversity influences the presence of van der Waals forces, hydrophobic effects and hydrogen bonding, in addition to the electrostatic forces already mentioned. Therefore, pH not only determines the ionic/neutral species ratio that influences the interaction with the surface of biosorbents (Xiao and Pignatello 2014), but also balances all the interactions specifically associated to the organic compounds. Therefore, quantitative analysis and interpretation of the interactions between biosorbents and organic pollutants are not straightforward (Healy and White 1978; Nelson and Schwartz 2013) and would require a dedicated review (Luthy et al. 1997; Aksu 2005; Shon et al. 2006; Higgins and Luty 2007; Richter et al. 2009; Kushwaha et al. 2013; Webster 2014; Van Son et al. 2015; Zhou et al. 2015; Christl et al. 2016).

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 Jianlong 2009; Javanbakht et al. 2014) mainly physical adsorption, ionic exchange, complexation, chelation, reduction or microprecipitation (Veglio and Beolchini 1997; Schiewer and Volesky 2000; Crini 2005).

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.

Despite the problems mentioned, a large number of studies report the correlation of the adsorption capacity with the number of protonated groups in the biomass. Lodeiro et al. (2008) studied the Cr(III)-binding capacity of three different types of biomass, the brown *Sargassum muticum* macroalgae, 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 potentiometrically. On the other hand, the complexation constants were determined and a very close value is obtained for the three materials ($\log K_{Cr} = 2.9$–3.1), that reinforces the hypothesis of the implication of the same functional group, e.g. carboxyl groups, in metal uptake. Barriada et al. (2009) studied the adsorption of Cd (II) and Pb (II) on bracken fern. Maximum uptake was found to be the same for both metals ($0.410\ \mathrm{mmol \cdot g^{-1}}$), which is very similar to the number of acidic groups determined for this material that was found to be $0.432\ \mathrm{mmol \cdot g^{-1}}$. 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, further supportive evidences for 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 (Figure 3.10) (Schiewer and Volesky 1995; Ravat et al. 2000; Reddad et al. 2002; Lodeiro et al. 2004, 2005a). At pH values below 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. 2004b).

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

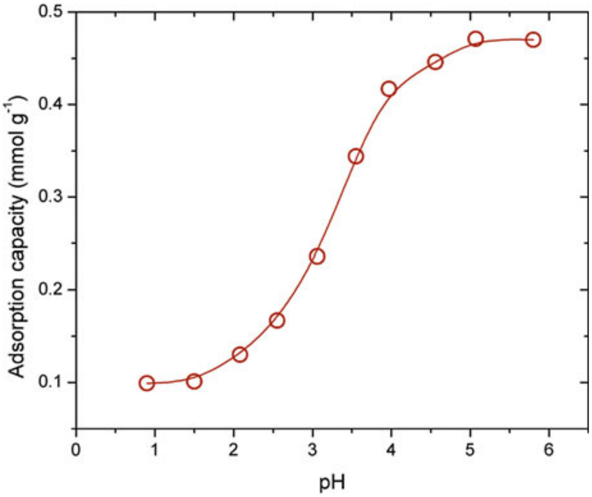

Fig. 3.10 Dependence of the Cd adsorption capacity of the macroalga *Cystoseira baccata* on pH. The circles represent experimental data points and the line guides the eye. The graph shows the typical S-shaped curve that supports evidence for the implication of acidic groups on metal binding

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 and Wong (1999) to Ni and Cu adsorption by several types of algae, assuming 1:2 binding stoichiometry. 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 attained through proton binding studies. Pagnanelli et al. (2005a) obtained similar results using the NICA model to reproduce the Cu and Cd biosorption experiments on olive pomace. 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. (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.

3.9 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 (Pagnanelli et al. 2000, 2004; Schiewer and Patil 2008a; Li et al. 2014). In conjunction with other analytical measurements such as calorimetric data or NMR, the acid-base characterization of biosorbents can provide significant information about the functional groups present in these substances, and the contribution of these groups to overall adsorption. 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; Lodeiro et al. 2012; Pagnanelli et al. 2013; Li et al. 2014), which is another interesting property of these materials and with important effects on the adsorption.

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 2008a). The analysis of these curves will provide the corresponding acid-base information of the substance under study. But it has to be kept in mind that any biosorbent can be considered as a heterogeneous mixture of multifunctional polymers. Consequently, the analysis of the titration curves is not as trivial as that obtained for a single, pure substance (Lenoir and Manceau 2010). Besides, being multifunctional biopolymers, 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 (Fig. 3.9).

Different techniques can be used to obtain acid-base information of substances, among others NMR measurements, UV-Vis spectrophotometric readings, conductivity measurements or calorimetric data (Gans et al. 1996, 2008; Bouanda et al. 2002; De Stefano et al. 2005). Nevertheless, potentiometry with glass electrode is the most important one, widely used especially in biosorbent acid-base analysis; most likely due to its simplicity and accuracy. Moreover, 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; that is the major change compared to a traditional titration. 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 (in fact, the evolution of the emf readings) is followed. The pH or emf and volume of titrant added constitute the starting data employed during analysis.

3.9.1 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, especially if the effect of the temperature is going to be analysed. 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. Nowadays the most common reference electrode is the Ag|AgCl electrode, either in a saturated chloride solution or at 3 M concentration chloride solution. 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, it has to be kept in mind that many of the biosorbents studied are rather soft materials, so 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. Figure 3.11 shows a typical potentiometric titration set-up.

Finally, another common procedure in potentiometric acid-base titrations, also for biomaterials, is the usage of an inert electrolyte (Bouanda et al. 2002; De Stefano et al. 2005; Barriada et al. 2009). 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. The inert electrolyte should be present at 0.1 M or more in order to buffer changes in the proton activity coefficient. 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 facilitates the subsequent derivation of the apparent equilibrium constants of the acidic groups involved in the acid-base equilibria.

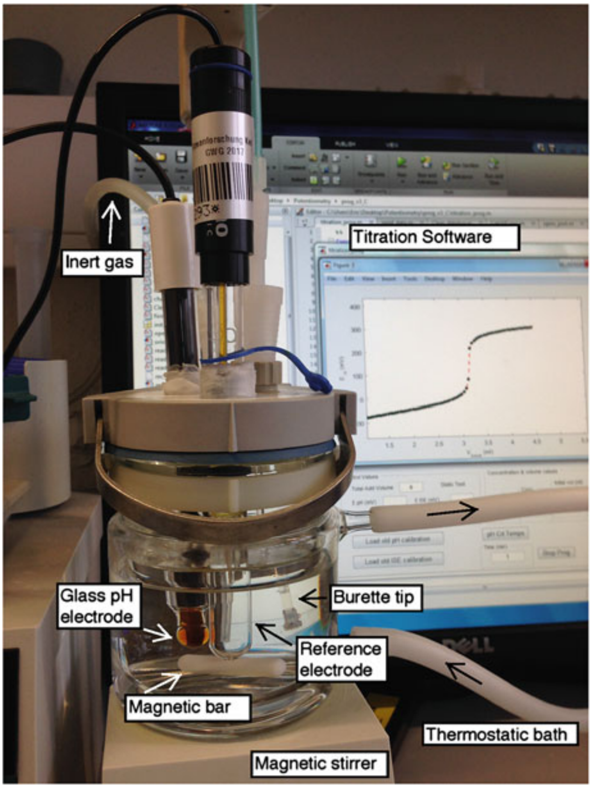

Fig. 3.11 Typical titration set-up for biomass acid-base properties determination. The experimental set-up is formed by a thermostated vessel, a pH glass electrode, a reference electrode, an inert gas bubbler and a burette for adding the titrant. Magnetic stirring is used to achieve a correct mixture of the biomass suspension

3.9.2 Calibrations

As it has been mentioned above, the most common procedure in potentiometric acid-base titrations consist of using an inert electrolyte. This electrolyte does not interact with the species being titrated, and buffers the ionic strength of the solution. In this situation, 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, at the same ionic strength that is going to be used in the titration of the biosorbent, where aliquots of a strong acid e.g. HCl 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:

$$E = E^* + p\,log[H^+] \tag{3.33}$$

where E is the electromotive force, E* is the so-called formal potential which encompasses the standard potential of the electrode system, the potential of asymmetry and the liquid junction potential; moreover, it also depends on the activity coefficient of the proton, a constant when fixed ionic strength solutions are used. 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 log [H^+] vs. E renders a straight line (May et al. 1982) with a slope that should not be very different from the theoretical value (59.16 at 25 °C). For every addition the concentration of protons is calculated as:

$$[H^+] = C_a \cdot \frac{v}{V_0 + v} \tag{3.34}$$

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. 3.34 together with the emf readings allow fitting of the experimental data to Eq. 3.33, 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, especially if the glass electrode has been stored dry for a considerable time. Frequent calibrations of a glass electrode will evolve to stable values of formal potential and slope, which in turn can be used to transform the readings of a biomass titration into values of free proton concentration, which are used in the calculation of the proton affinity constants of the functional groups present in the biomass.

Working with the free proton concentration scale ($p[H^+] = -\log[H^+]$) (May et al. 1982; Fiol et al. 1992; Brandariz et al. 2001, 2004) might look cumbersome compared to working with pH ($pH = -\log a_{H^+}$, where a_{H^+} stands for activity of protons). However, it has to be kept in mind that pH calibration of glass electrodes using the commercially available pH buffers is done in an unknown ionic media that is going to be totally different from the media used in the biomass titration. Hence an unknown uncertainty regarding proton activity coefficient will be introduced using the pH scale. Thus, use of free proton concentration scale is recommended.

3.9.3 Measurements

Although the potentiometric titrations of biosorbents are very similar to acid-base titrations of simple substances, some important differences have to be discussed. As has been indicated above, a biosorbent titration is done with a suspension of the biosorbent. Therefore, a heterogeneous mixture is used rather than working with a homogenous solution, as is the case of a simple substance titration. This fact makes stirring an important factor, since the biosorbent will tend to separate from solution by gravity. Furthermore, if the biosorbent is decanted at the bottom of the titration vessel it might not react with the titrant added, or it will take longer to react. 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. Depending on the nature of the sorbent and the environment where it is found, the functional groups that constitute the active sites of the material can be in different protonation states. This might make it difficult to interpret the potentiometric titration data, since it can significantly influence in the number of total acid sites determined. 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 before proceeding with the titration (Rey-Castro et al. 2003; Schiewer and Patil 2008a; Barriada et al. 2009). Other researchers 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. Of course, this description corresponds to a “forward” titration, where the pH of the mixture is progressively increased by addition of a base of known concentration. It is also possible to do “backward” titrations, starting with the biomass in a fully deprotonated state, and perform the titration adding as titrant an acid of accurately known concentration.

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. As a consequence of this drift in the glass electrode readings, 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. Dealing with such long times, and having to wait for stable readings, biomass titrations are time-consuming, and therefore 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 data analysis (Barriada et al. 2009; Lodeiro et al. 2012).

3.9.4 Data Analysis

The analysis of the data obtained during a titration is usually based on a charge balance equation; that is, the electroneutrality condition: the charges of all the positive species has to be compensated by the charge of the negative species. As an example, 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:

$$[Na^+] + [H^+] - [Cl^-] - [OH^-] + Q = 0 \tag{3.35}$$

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 Eq. 3.35 can be easily transformed into charge-pH or master curves (see Sect. 3.6).

The concentrations of the cations and anions from the background electrolyte are not considered here since they mutually cancel each other out. If the glass electrode has been calibrated in the free proton scale, the emf readings can be easily transformed into proton concentration [H^+] (Eq. 3.33). Also, 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 easily calculated from knowledge of 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 (Fig. 3.11).

In fact, this is a procedure to determine the potential of zero charge of the biosorbent. If the titration is made in the same conditions but for different masses of biosorbent, a plot of pH *versus* charge should cross at a single point corresponding to the potential of zero charge. Since at this potential the biomass shows a neat zero charge at its surface, this point will be independent of the mass of biomaterial used in the titration and the intersection of the curves will provide the pzc value. Figure 3.12 shows a typical plot that can be used to determine the pzc value of a substance. In this case instead of plotting the charge *versus* the pH, a plot of pH *versus* titrant added is represented. In any case, the intersection of the curves indicates the pH at which the material used has a zero net charge in its surface.

If the charge so calculated corresponds to the charge of an acidic group once it gets deprotonated, according to the following equilibrium:

$$R - AH \rightleftharpoons R - A^- + H^+ \tag{3.36}$$

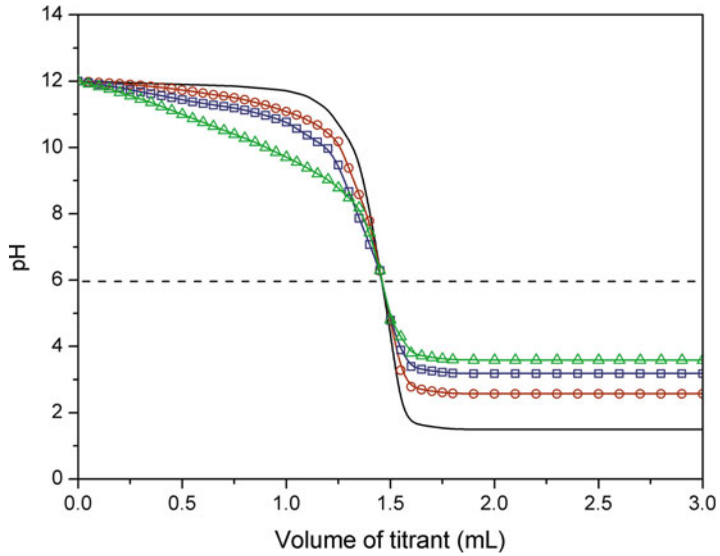

Fig. 3.12 Simulated acid-base titration of a biomaterial using different masses: e.g. 10 (red), 25 (blue) and 50 (green) g·L^{-1}. The black line represents a control titration without biomass. The intersection point, in this case ca. pH 6, corresponds to the potential of zero charge (pzc) of the biomaterial under study. At this pH, the biomass should show a neat zero charge at its surface, so this point is independent of the mass of biomaterial

then, the dissociation degree, α, can be calculated as:

$$\alpha = \frac{[R - A^{-}]}{[R - AH]_{tot}} = \frac{Q}{C_A} \tag{3.37}$$

where $[R - AH]_{tot} = C_A$ represents the total number of acidic sites present in the biosorbent, which can be calculated from the inflection point of the titration curve, or estimated by other means such as the barium hydroxide method (Fukushima et al. 1999).

The apparent protonation constant (K_{app}) of the acidic groups involved in the equilibrium can then be computed with Eq. 3.25, which is based on a modification of Henderson-Hasselbach equation (Katchalsky and Spitnik 1947; De Stefano et al. 2005). The plot of $p[H^{+}]$ vs. $log\left(\frac{1-\alpha}{\alpha}\right)$ should be a straight line that intersects (i.e. when α=0.5) the x axes at $p[H^{+}] = \log K_m = \log K_{app}$.

The procedure described above corresponds to a situation where only one major functional group (e.g. carboxylic acid) seems to be present in the biomass, i.e. only one inflection point is observed in the titration curve. If more than one inflection point are observed in the curves, different approaches are required. Sometimes a continuous affinity spectra model is used; in that case, the affinity constants of the functional groups present in the biomass are considered to vary in a continuous range of values. A discrete values model can be also used, where between 2 and 4 types of functional monoprotic acidic sites are modelled in order to described the experimental curves. Generally speaking, differences regarding to experimental curve fitting between the continuous model and a 3 sites model are minimal. Titrations of biomass with several inflection points are usually well described considering strong acidic sites with apparent pK values below 4, weak acidic sites with pK values between 4 and 7 and very weak acidic sites with pK values above 7. Correct identification of these functional sites is more complicated, considering the very heterogeneous nature of the biomaterials, but quite often the strong acidic sites are associated with sulfonate or phosphoric functional groups, weak sites are associated with carboxylic moieties and very weak with phenolic or amine groups present in the biopolymers.

3.10 Conclusions and Future Research Needs

1. 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.
2. 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.
3. 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.
4. 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.
5. 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.
6. 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.

7. 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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