Thermodynamic and Kinetic Aspects on the Biosorption of Cadmium by Low Cost Materials: A Review

Pablo Lodeiro, Roberto Herrero, Manuel E. Sastre de Vicente*

Departamento de Química Física e Enxeñería Química I, University of A Coruña,

Alejandro de la Sota 1, 15008 A Coruña, Spain.

*Corresponding author e-mail: eman@udc.es; Phone: (34) 981 167000 Fax: (34) 981 167065

ABSTRACT

Cadmium is internationally recognized as an important pollutant in the environment and different methods (chemical precipitation is the most commonly used) for its removal from wastewaters have been reported in the literature. Those methods are in most cases oriented to situations with high concentrations of the pollutant. Thus, alternative removal/recovery methods are being considered for very low concentrations all based in the metal-sequestering properties by biosorption ("passive" adsorption) of several natural materials of biological origin.

In this review we have considered the biosorption of cadmium onto biomaterials from a physicochemical, thermodynamic and kinetic perspective. The thermodynamic one is based on the characterization of the interactions of the binding sites of the biosorbents with cadmium species in aqueous solution. Traditionally, this approach has been quantified using different kind of isotherms. In addition, that description must be completed taking into account the electrostatic effects, influenced by pH and ionic strength, associated to the negative charge developed in most cases by the biomaterial. The other point of view in this review is the kinetic one, which is necessary for a full physicochemical description of the sorbate/biosorbent system. Consequently, an updated description of the various approaches commonly employed in kinetic studies in biosorption has been carried out.

Keywords: Biosorption, cadmium, isotherms, kinetics, acid-base properties

TABLE OF CONTENTS

1. Cadmium in the environment

According to EPA (US Environmental Protection Agency), cadmium is a chemical that is one or more of the following: highly acutely toxic, neurotoxic cholinesterase inhibitor, known/probable carcinogen, known groundwater pollutant or known reproductive or developmental toxicant. The International Agency on Cancer Research has recently classified cadmium as carcinogen. The impact of cadmium on aquatic organisms depends on a variety of possible chemical forms of cadmium which can have different toxicities and bioconcentration factors.

Also the European Pollutant Emission Register (EPER), which comprises 50 substances which have to be reported by industrial facilities if their emissions exceed certain threshold values, establishes for cadmium that the limits for air, water and land are, respectively, 0.01, 0.005 and 0.005 t. per year.[1] In Europe, total emissions of cadmium and its compounds per year are 23.54 t. to air, 12.35 t. direct to water and 1.68 t. indirect to water by transfer to an off-site waste water treatment.

Most of these emissions, about 60-70 % are originated from metal industry and metal ore roasting or sintering installations and installations for the production of ferrous and non ferrous metals. Typical industrial uses of cadmium are NiCd batteries, as cadmium hydroxide, cadmium pigments (cadmium sulphide and cadmium sulphoselenide), cadmium stabilisers as cadmium laurate and cadmium stearate, coatings against corrosion, alloys, fertilizers and pesticides and other minor uses as, for example, cadmium telluride and sulphide in solar cells.

In the Dangerous Substances Directive 76/464/EEC, cadmium and its compounds are among the 129 so-called "black-list" substances which were considered to be so toxic, persistent or bioacumulative, that efforts to control chemical releases and prevent pollution should be given the highest priority.

Different treatment methods for cadmium removal from wastewaters have been reviewed by Poon.[2] Table 1 in that paper reports cadmium concentrations from industrial and municipal wastewaters ranging from 0.001 to 5000 ppm depending on the source.

The various methods reported are: chemical precipitation, hydroxide precipitation, carbonate precipitation, sulphide precipitation, sodium borohydride precipitation, hydrogen peroxide oxidation-precipitation. It is well known that metal precipitation can generate a large amount of cadmium sludge classified as dangerous waste in most regulations, so its appropriate disposition constitutes a serious environmental and economical problem for the involved industries. Other described methods are electroflotation, ion exchange and adsorption, especially with active carbon, and foam flotation. An important conclusion of Poon´s review, after cost comparisons of the processes, states that assuming that sludge treatment and disposal are operable, alkaline precipitation is by far the most cost effective treatment process. However, ion exchange and carbon adsorption processes offer an opportunity to recover cadmium and water for reuse which could offset some of the costs. As it can be seen, there are different methods for the removal of cadmium from wastewaters, specially when they are present in high concentrations; however, identifying practical and cost -effective ways of removing such contaminant at very low concentrations is much more difficult. In fact, suitable processes at high concentrations are often either ineffective or cost prohibitive when applied to dilute wastes with low heavy metal concentrations. For these reasons, alternative metal removal and/or recovery methods are being considered all based on the metal-sequestering properties of several natural materials of biological origin. Certain types of biomass can retain relatively high quantities of metal ions by "passive" adsorption. This process is known as biosorption in contrast to bioaccumulation, an active mode of metal accumulation by living cells which depends on the metabolic activity of the cell.

2. Comparison of maximum cadmium uptakes by low cost materials

In this review, an extensive list of sorbent literature has been compiled to provide a summary of information on a wide range of potentially low-cost sorbents. A sorbent can be assumed as low cost, if it requires little processing, it is abundant in nature or it is a by-product or waste material from another industry. Cost is an important parameter for comparing the sorbent materials. However, cost information is seldom reported and the expense of individual sorbents varies depending on the degree of processing required and, specially, on local availability, so cost comparison are difficult to carry out.

It is important to note that the adsorption capacities of the adsorbents depend heavily on the characteristics of the individual adsorbent, on the extent of chemical modifications and on the experimental conditions such as pH, metal concentration, competing ions, etc. Table 1 collects cadmium adsorption capacity of a great amount of adsorbents. The table fails to report specific test conditions because not always this information is found in literature. The data incorporated in the table correspond with the optimum conditions to achieve maximum adsorption and the $Q_{max,Cd}$ value is the result obtained to fit experimental data to Langmuir isotherm.

According to Table 1, it can be observed that there are potent biosorbent materials among easily available biomass types as algae, fungi, bacteria, agricultural waste products, lignin, chitin/chitosan, ...

Biomass from brown marine macroalgae is a renewable biological resource, which is available in large quantities and can form a good base for the development of biosorbent material. Brown algae contain high concentrations of alginate and sulphated polysaccharides. The major component of the alginate is alginic acid, a polymer composed of unbranched chains of 1,4-linked β-D-mannuronic and α-L-guluronic acids.[3] Both uronic acids occur in varying portions and different quantities in samples of polysaccharides taken from different

algal species. These parameters can also differ according to the age, season and origin of the alga. Other negatively charged functional groups, such as the sulphonate groups of fucoidan, also contribute to Cadmium complexation although it is difficult to evaluate the absolute role that these polymers play in determining the metal uptake. Fucoidan is a branched polysaccharide sulphate ester with L-fucose building blocks which are predominantly $\alpha(1\rightarrow2)$ linked.[4]

Cadmium adsorption capacities as high as 2.52 $mmol \cdot g^{-1}$ can be found for *Lyngbya taylorii*,[5] 1.91 $mmol \cdot g^{-1}$ for *Ascophyllum nodosum* or 1.17 $mmol \cdot g^{-1}$ for *Sargassum natans* [6] while average values for brown algae are about 0.6-0.9 $mmol \cdot g^{-1}$. Certain increase in adsorption capacity can be observed due to crosslinking or simple chemical pretreatment of the biomass. While pretreatment will increase cost, some kind of pretreatment or immobilisation of the biomass may be necessary to create a material with the right size, mechanical strength, rigidity and porosity for use in operations typical of chemical engineering. The effects of different kinds of pretreatment on the adsorption capacity are shown in Table 1.

The sequestering capacity of metallic species by microbial biomass (fungus and bacteria) is mainly due to their cell wall. Various polysaccharides are the main constituents of the fungal cell wall. They are often complexed with proteins, lipids and other substances. The fungal cell wall presents a multilaminate, microfibrillar structure organized in two phases: an outer layer consisting of glucans, mannans or galactans and an inner microfibrillar layer consisting of chitin chains, sometimes of cellulose chains or, in certain yeast, on noncellulosic glucan. Pigments, polyphosphates and inorganic ions are also found in the fungal cell wall.

On the other hand, bacterial biomass can be clasified in two main categories based on their cell wall structure: gram positive and gram negative bacteria, that are differentiated by the thickness of their peptidoglycan layer (linear polimer of alternating glucosamine and

muramic acid with peptide side chains). The gram positive cell wall is thicker than the gram negative, and also contains teichoic and teichuronic acids; all these components provide the anionic groups (carboxyl, phosphodiester, etc.), where metallic species can be retained, mainly by three types of different mechanism: adsorption, microprecipitation and nucleation. Gram negative bacteria posses a much thinner peptidoglycan layer and it does not contain teichoic and teichuronic acids, which implies a reduction in metal binding capacity, as compared to gram positive.

It is convenient to distinguish between metabolically mediated mechanism uptake process (bioacumulation) and nonspecific binding of metal to the cell surface (biosorption), which take place with dead microbial material or its cellular products. Dead cells accumulate heavy metals to an equal or greater extent than living cells. The use of dead rather than live biomass eliminates the problems of waste toxicity and nutrients requirements. Moreover, large quantities of waste microbial biomass are produced in many industries. Fungi are used in fermentation industries to produce varied metabolites such as antibiotics, steroids, industrial chemicals, enzymes, etc., while bacteria, the most abundant and versatile of the microorganisms, can be obtained as a waste product of these processes. Thousand of tons of residual biomass are produced each year, incineration is the main way of destroying these by-products. Some types of industrial fermentation waste biomass are excellent cadmium biosorbents and, in general, metal biosorbents. Microbial biomass of *Bacillus laterosporus* presents uptakes of 1.42 $mmol \cdot g^{-1}$,[7] *Aeromonas caviae* of 1.38 $mmol \cdot g^{-1}$.[8] Typical values for fungus *Rhizopus*, *Penicillium* or *Aspergillus*, and for bacteria *Streptomyces* or *Pseudomonas*, are compressed between 0.2-0.6 $mmol \cdot g^{-1}$, depending also if they are as free cells or immobilized biomass. For industrial application, a freely suspended microbial biomass has several disadvantages, as low density and mechanical strength, which may make biomass/effluent separation difficult. Fungal biomass has been immobilized using gelatin,

casein and other polypeptidic material or by crosslinking using reagents such as formaldehyde, glutaric dialdehyde, divinylsulfone and formaldehyde-urea mixtures.

Another material employed as potential cadmium adsorbent is chitin, poly (β-(1→4)-2-acetamido-2-deoxy-D-glucopyranose, and its partially deacetylated form, chitosan. Chitin is very abundant in nature, and it is found in the shell of crustaceans and in the cell walls of some fungi. Chitosan can be produced chemically from chitin and it is found naturally in some fungal cell walls. Chitosan is inexpensive and abundant, and it is highly adsorbent for heavy metals. Several studies have demonstrated that its interactions with metals are always much more important compared to those of chitin due to the higher number of free amine groups in the chitosan molecule. In fact, Dzul-Erosa [9] found adsorption capacities as high as 1.33 $mmol \cdot g^{-1}$ for chitosan, while with chitin only 0.14 $mmol \cdot g^{-1}$ were obtained.[10] Since chitosan can be dissolved in acidic media, crosslinking of chitosan is necessary for the purpose of insolubilization. The capacity of metal adsorption is known to become relatively small due to crosslinking between the polymer chains of chitosan as metallic ions normally adsorb onto the amino and hydroxyl groups of chitosan.

Another hereterogeneous group is formed by agricultural by-products. There are very different materials which present also very different adsorption capacities. In Table 1, it appears kraft lignin with a value of 1.31 $mmol \cdot g^{-1}$ [11] or carboxymethylated lignin with a value of 0.60 $mmol \cdot g^{-1}$.[12] Severe differences can be also found comparing the cadmium adsorption capacities of bean peel, peas peel and medlar peel with uptake values of 1.31, 1.06 and 0.87 $mmol \cdot g^{-1}$, respectively.[13] Other low cost materials obtained as agricultural by-products are, for example, orange waste which is able to sequester 1.10 $mmol \cdot g^{-1}$,[14] grape stalk waste 0.25 $mmol \cdot g^{-1}$,[15] sugar beet pulp 0.22 $mmol \cdot g^{-1}$,[16] rice husk from 0.08 to 0.18 $mmol \cdot g^{-1}$ depending of the treatment,[17] Brazil nutshells 0.17 $mmol \cdot g^{-1}$,[18] tree fern 0.15

mmol·g^{-1}.[19] Table 1 collects more of these materials with similar or lower adsorption capacities.

The common feature of all the above mentioned materials is the presence of natural biopolymers in their structure. These biopolymers represent an interesting and attractive alternative as adsorbents because of their particular structure, physico-chemical characteristics, chemical stability, high reactivity and excellent selectivity towards metals, resulting from the presence of chemical reactive groups as carboxyl, hydroxyl, sulphate, acetamido or amino functions in polymer chains. Polysaccharides are abundant, renewable and biodegradable resources and they have capacity to associate by physical and chemical interactions with a wide variety of metal ions. Hence, adsorption on materials containing polysaccharides can be a low-cost procedure of choice in water decontamination for extraction and separation of metals, and a useful tool for protecting the environment. The increasing number of publications on adsorption of toxic compounds by modified polysaccharides shows that there is an increasing interest in the synthesis of new low-cost adsorbents used in wastewater treatments. A recent review [20] shows the new developments in the synthesis of adsorbents containing polysaccharides, in particular, modified biopolymers derived from chitin, chitosan, starch and cyclodextrin.

As a matter of comparison, adsorption capacities of commercial ionic exchange resins such as amberlite RI-120, with 0.90 mmol·g^{-1} of cadmium uptake [21], or activated carbon, with 0.07 mmol·g^{-1} [22], are also included.

Finally, Table 1 also contains adsorption capacities of some mineral materials (not considered as biosorbents) which are often used as low cost materials for the adsorption of metal ions as zeolites or clays. Basically, zeolites are naturally occurring crystalline aluminosilicates consisting of a framework of tetrahedral molecules, linked with each other by shared oxygen atoms. Clays are also important inorganic components in soil. Their

sorption capabilities come from their high surface area and exchange capacities. The negative charge on the structure of clay minerals gives clay the capability to attract metal ions. There are three basic species of clay, smectites (such as montmorillonite), kaolinites and micas. The adsorption capacity of these materials can vary strongly. Dal Bosco found a value of 0.89mmol·g^{-1} for the brazilian zeolite Scolecite [23] while values as low as 0.05 mmol·g^{-1} were found for Na-Montmorillonite.[24]

Other collections of adsorption data by low cost materials can be found in some review papers previously published such as those of Volesky,[25] Veglió,[26] Bailey,[27] Sag,[28] Babel [29] or Crini.[20, 30]

3. Thermodynamics of the interactions of cadmium and protons with biosorbents

3.1 Acid-base properties

Most materials with sorbent properties contain natural biopolymers which complexation study is hindered by several effects commonly present in these macromolecular systems. Generally, a biomaterial has a relatively high number of complexing sites. Therefore, the number of chemical species involved in the system may become enormously large and the description of the system may be done in terms of a distribution of species. Even though the binding reaction takes place between the inorganic cation and each complexation site, several "secondary" effects may influence the overall complexation process in greater or lesser extend:[31]

- Polyfunctionality. The binding sites can be chemically heterogeneous in various ways: the coordinating groups may be of different type (the major binding sites are usually carboxylic and phenolic groups, although also nitrogen and sulphur containing groups may

play a role), and/or they can show different electronic (aliphatic chains, aromatic rings) or steric environments.

- Conformational changes. The steric conformation of the complexants can vary with the chemical conditions of the medium, such as pH, ionic strength or amount of bound cation. For instance, linear polyelectrolytes may experiment conformational transitions depending on the degree of dissociation, as a consequence of the electrostatic repulsions among charged groups along the molecule chain.

- Polyelectrolytic effect. Many of the biomaterials complexing sites are often charged at a given pH, ionic strength, and cation concentration. Therefore, they carry a high local charge concentration, which influences the stability of the complexes. It can be considered, for instance, the particular case of proton dissociation from an initially uncharged polyprotic acid. As the dissociation proceeds, the net charge becomes progressively more negative, and therefore each proton experiences a larger net attractive Coulombic force than the previous one, which means that the apparent dissociation constant decreases, i.e. the polyacid becomes weaker.

Sorption equilibrium is established when the concentration of a sorbate in a bulk solution is in dynamic balance with that of the sorbent interface. The degree of the biosorbent affinity for the sorbate (metal) determines its distribution between the solid and liquid phases. The analysis of equilibrium data is important to develop a technology based on biosorption using mathematical models, which could be used for the quantitative description of the results. The equation parameters and the underlying thermodynamic assumptions of these equilibrium models should be capable of predicting metal biosorption, reflecting the mechanism of the sorbate uptake and the influence of variables such as pH, ionic strength, presence of competing cations, etc. However, in most cases equilibrium models are used

empirically as functional expressions capable of simulating favourable equilibrium uptake curves if environmental parameters, such as pH, are carefully controlled during experiments.

The starting point in the development of a physical-chemical model for the description of metal ion binding to a biosorbent is the description of proton binding as a function of pH in 1:1 electrolytes. The proton binding equilibria are studied through potentiometric titration of the acid-treated biomass, which allowed to obtain the maximum amount of acid functional groups from the volume at the equivalence point.

Moreover, the amount of proton bound can be calculated from the acid and base additions by means of charge balance considerations [32]:

$$Q_H = Q_{\max,H} - \frac{V_T}{m_s}\left([H^+] + \frac{V_b C_b - V_a C_a}{V_T} - \frac{K_w}{[H^+]} \right) \quad (1)$$

where V_i, C_i are the volume and concentration of the acid and base added (subscripts *a* and *b* refer to acid and base, respectively), V_T is the total volume in the titration vessel, K_W is the ionic product of water, and $Q_{\max,H}$ is the total amount of titratable groups, calculated from the equivalence point of the titrations.

The proton dissociation of an acid group in a macromolecule can be represented by the formal reaction:

$$-AH = -A^- + H^+ \quad (2)$$

For this reaction, a conventional dissociation constant, K_a, can be defined as:

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

Note that analytical concentrations (denoted by square brackets) are used in Eq. 3 rather than activities, and hence K_a is not a true thermodynamic dissociation constant, but an apparent constant. This equation can be written as:

$$pK_a = pH - \log\frac{\alpha}{1-\alpha} \quad (4)$$

which is formally identical to the well-known Henderson-Hasselbach equation.

In Eq. 4 α represents the degree of dissociation of the macromolecule, defined as:

$$\alpha = \frac{[-A^-]}{[-A^-]+[-AH]} \quad (5)$$

The modified Henderson-Hasselbach equation, which is equivalent to Langmuir-Freundlich equation, is widely used for the description of the dependence of the protonation constants of polyelectrolytes on the degree of dissociation. This model, although purely empirical, constitute an useful tool for summarizing, in an accurate and convenient way, the experimental thermodynamic information regarding the acid-base and complexation equilibria under different conditions (pH, ionic strength, temperature, etc). Katchalsky and coworkers found that the potentiometric behaviour of diluted solutions of polymeric acids can be formally described by two empirical constants, pK_m and n, by means of the following equation:[33]

$$pH = pK_m + n\log\frac{\alpha}{1-\alpha} \quad (6)$$

where $pK_m = pK_a$ for $\alpha = 0.5$, and $n>1$. Both constants can be obtained by the fit of experimental data to Eq. 6. They depend on the type of polyacid, but are almost independent of the molecular weight. They vary with ionic strength, n approaching 1 (the value for monomeric ligands) and pK_m decreasing to a limiting value for high ionic strengths.

This equation has been theoretically interpreted on the assumption that the deviation from the titration behaviour of monobasic acids is due to the work expended in the removal of the hydrogen ion from the field of the ionized groups, as well as to the work performed by the polymer molecule on stretching by electrostatic forces. By combining Eq. 4 and 6 the relationships between pK_a and α or pH can easily be obtained.

The extension of the model from a single component (proton) to the general multi-component case (competitive ion binding) is a major challenge. The first common assumption in most physicochemical models is that, in principle, all specifically bound cations including proton should be able to compete for the same sites. In this aspect, the native biomass represents an additional problem, since protons and cadmium ions must compete not only with each other, but also with the light metal ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, etc.) already present in the cell wall as counterions of different groups. Crist et al.[34-38] demonstrated, through careful mass balances in different biosorption processes, that these ions are exchangeable with protons. In order to avoid this effect and simplify the system, normally, only the binding data obtained with acid-treated biomass (which is supposed free of exchangeable metals) are used for modelling purposes.

3.2 Isotherms

It should be mentioned that, in most cases, the capacity of a given biomass to sequester heavy metals has been traditionally quantified (see references in Table 1) using the Langmuir, Freundlich, Langmuir-Freundlich or some alternative simple models.[39] However, these simple models were developed under many assumptions that are well known to not be met in the case of biosorption. The main reason for the extended use of these isotherms is that they describe satisfactorily experimental data. Although they can not be used for predictions and they do not incorporate external parameters, such as pH or ionic strength, they include constants that are easily interpreted and allow to compare the behaviour of different biosorbents.

Table 2 shows the most common isotherm equations used in biosorption. The amount of metal sorbed at equilibrium, Q, which represents the metal uptake, can be easily obtained from the difference in metal concentration in the aqueous phase before and after adsorption, according to the following equation:

$$Q = \frac{V \cdot (C_i - C)}{m} \tag{7}$$

where V is the solution volume, C_i and C are the initial and equilibrium concentration of metal in solution, respectively, and m is the mass of dry biosorbent.

The adjustable parameters of the equations showed in Table 2 are: Q_{max}, that represents the maximum adsorption capacity; b, an affinity parameter (a high value indicates a steep desirable beginning of the isotherm reflecting the high affinity of the biosorbent for the sorbate); n is an empirical parameter that varies with the degree of heterogeneity and K_f is related to biosorption capacity. One must be aware that these empirical parameters are conditional values, in the sense that they are valid only for the experimental conditions under which they have been obtained.

In order to account for stoichiometry, description site heterogeneity and competition phenomena among different metallic species, or with protons (pH effects), modified Langmuir sorption models can be used. If it is considered a reaction between different A_i biosorption sites and j metals in solution, with equilibrium constants and concentrations of K_j and C_j, respectively, a general Langmuir expression (Eq. 8) can be obtained combining mass balance and equilibrium constants:[40]

$$Q_j = \sum_i [A_i]_{tot} \frac{K_{ij} C_j}{1 + \sum_j K_{ij} C_j} \tag{8}$$

If ideal sorption behaviour is presumed, these adjustable parameters can be separately obtained from different single metal experiments or can be fitted using multicomponent data.

Several examples of the application of these kind of models can be found in the works of Pagnanelli et al.,[41] Lodeiro et al. [42] or Schiewer and Wong,[43] who proposed a competitive Langmuir isotherm (Eq. 9) involving one type of binding site and one type of metal ion, that defines the stoichiometry ratio for proton/metal competition, 1:1 (n=1) or 1:2 (n=0.5) (Figure 1).

$$Q = n \cdot Q_{\max,H} \frac{(K \cdot C)^n}{1 + K_H \cdot C_H + (K \cdot C)^n} \tag{9}$$

Interactions of cadmium and other heavy metals onto different sorbent biomaterials have been mainly described not only in terms of complexation but in terms of an ion exchange reaction, evidenced by the fact that for each heavy metal ion sorbing an equivalent quantity of protons and/or other metal ions appears in solution.[34, 37, 38, 40, 44-48] However, certain controversy exists with regard to the relative weight (participation) of both complexation and/or ion exchange for each particular system,[34, 40, 44, 46] because ion-exchange does not completely and accurately describe the biosorption phenomenon, due to the fact that the cation-exchange capacity of the biomass increases with increasing pH, whereas the stoichiometry of the reaction varies with increasing metal concentrations, and therefore, in addition to ion-exchange, at least a reaction in which a metal cation reacts with a free site should be also considered.[4] In certain cases, surface precipitation has been also reported.[49]

The NICA competitive isotherm (non ideal, competitive and thermodynamically consistent adsorption) represents a great improvement with respect to these simpler descriptions of data. It addresses heterogeneity and stoichiometry effects and it was initially developed for humic and fulvic acids.[50, 51]

The basic NICA equation for the overall binding of species *i*, in the competitive situation is:

$$\theta_i = \frac{\left(\tilde{K}_i c_i\right)^{n_i}}{\sum_i \left(\tilde{K}_i c_i\right)^{n_i}} \frac{\left[\sum_i \left(\tilde{K}_i c_i\right)^{n_i}\right]^p}{1 + \left[\sum_i \left(\tilde{K}_i c_i\right)^{n_i}\right]^p} \tag{10}$$

where θ_i is the coverage fraction of the species *i*, $\tilde{K}_i$ is the median value of the affinity distribution for species *i*, *p* is the width of the distribution (usually interpreted as a generic or

intrinsic heterogeneity seen by all ions) and n_i is an ion-specific non-ideality term. Strictly speaking, c_i should be the local concentration of species i at the binding site, i.e., the bulk concentration (or activity) corrected for the double layer effect (for instance, the concentrations in the Donnan phase).

The following normalization condition is used to calculate the amount of species i bound, Q_i:

$$Q_i = \theta_i \left({}^{n_i}\!/\!_{n_H} \right) Q_{\max,H} \tag{11}$$

where $Q_{\max,H}$ is the maximum binding capacity for protons, which can be calculated from the equivalence point of the acid-base titrations in absence of heavy metal.

The ratio n_i/n_H has been interpreted by Kinniburgh et al. [50] in terms of stoichiometry and cooperativity. When this ratio is less than one, then the maximum binding of species i is lower than the total amount of sites (defined as the amount of titratable protons), which would be a consequence of some degree of multi-dentism. On the other hand, a value of n_i/n_H greater than one would reflect some degree of cooperativity. Finally, if n_i/n_H =1, it can be demonstrated that the maximum proton/metal exchange ratio is one.

Its is easily seen that if $n_i=n_H$ =1, then the NICA isotherm reduces to the generalized (multicomponent) Langmuir-Freundlich isotherm:

$$\theta_i = \frac{\left(\tilde{K}_i c_i\right)}{\sum_i \left(\tilde{K}_i c_i\right)} \frac{\left[\sum_i \left(\tilde{K}_i c_i\right)\right]^p}{1+\left[\sum_i \left(\tilde{K}_i c_i\right)\right]^p} \tag{12}$$

Note also that if only the proton binding is considered (i.e., absence of competing ions) in Eqs. 11 and 12 , then the Langmuir-Freundlich isotherm is recovered:

$$Q_H = Q_{\max,H} \frac{\left(\tilde{K}_H c_H\right)^{m_H}}{1+\left(\tilde{K}_H c_H\right)^{m_H}} \tag{13}$$

where this time the heterogeneity parameter m_H describes the combined effect of n_H and p ($m_H = n_H \cdot p$). In the case of a homogeneous system (no chemical heterogeneity), m_H =1 and then the Langmuir isotherm is obtained.

The NICA model constitutes a powerful tool for the description of biosorption process, it is able to describe different types of experiments (metal sorption, acid-base titrations and influence of pH on biosorption), with great accuracy and a relatively small number of parameters simultaneously (Figure 1).[32, 41, 42, 52, 53] However, despite the obtained encouraging results, the knowledge of the geometric parameters that determine the electrostatic description of the system would be required in order to derive the intrinsic binding parameters (i.e., independent of the bulk ionic strength).[54]

3.3 Electrostatic effects

Despite the great utility of the previous models, they do not provide much insight into the physical chemistry of the cation-biosorbent binding equilibria. The empirical parameters are not straightforwardly related to the characteristic properties of the macromolecules, such as size or charge distribution. Another drawback of these simple models is that they do not include explicitly the electrostatic effect, which constitutes one of the most remarkable features of polyelectrolytic systems.

In general, the physicochemical effects mentioned above are coupled, that is, they occur simultaneously. For instance, the competitive equilibria of two particular cations depend on the charge of the macromolecule (i.e., on the proportion of ionised sites), and this, in turn, depends on the amount of bound cations. Nevertheless, it is generally assumed that, under certain conditions, the relative contribution of each effect can be accounted for by means of a suitable model, as an example, an electrostatic model is employed in conventional treatments of the polyelectrolytic effect in order to obtain a set of intrinsic binding constants (master curve) that only depend on the chemical heterogeneity.

Taking into account that, in most cases, a negative charge associated to the dissociation of acidic groups of biomaterials is developed, the interactions of these complex systems with their environment, specially with metals, are going to be necessarily dependent both on the acid-base properties of the biomaterial and on the metal speciation in solution; so variables as pH, ionic strength [55] or metal/site ratio are very relevant and they will determine the relative importance of the observed effects, mainly those associated to electrostatic interactions.

In general, the value of pK_a is a function of pH, in contrast to what happens with simple ligands. In monofunctional polymers, the deviations from ideality are usually ascribed to electrostatic effects (apart from conformational effects). Therefore, we can consider two contributions to the overall standard free energy change of the dissociation process:

$$\Delta G_{\text{diss}} = \Delta G_{\text{int}} + \Delta G_{\text{elec}} \tag{14}$$

where ΔG_{int} represents the chemical free energy due to the reaction of the functional group itself and ΔG_{elec} represents the coulombic free energy due to the electrostatic interactions between the proton and the charges of the polyanion. For the calculation of ΔG_{elec}, we can consider a thermodynamic cycle involving the following steps:[56] discharge of the macromolecule, dissociation of the uncharged species and, finally, charge of the de-protonated macromolecule

$$\begin{array}{lcll} AH^{(Q-1)-} & = & A^{Q-} + H^{+} & \Delta G_{\text{diss}} \\ \downarrow & & \uparrow & \Delta G_{\text{elec}} \\ AH_{(\text{discharged})} & = & A_{(\text{discharged})} + H^{+} & \Delta G_{\text{int}} \end{array} \tag{15}$$

where Q represents the overall charge of the macromolecule. Note that in Eq.15 the macromolecule is considered as a whole, whereas in Eq. 2 only the dissociation reaction taking place at an acid site is considered.

The free energy change for the global discharge-charge process is then calculated as:

$$\Delta G_{elec} = N_A \int_{-(Q-1)e}^{-Qe} \psi_0(q)dq \tag{16}$$

where $\psi_0(q)$ is the electrostatic potential at the reaction site. If Q >> 1 (that is, when the polyelectrolyte is not close to neutrality), it can be assumed that $\psi_0(q)$ remains approximately constant over the range of the integral, so that:

$$\Delta G_{electrostatic} = -F\psi_0 \tag{17}$$

The physical interpretation of Eq. 17 is that it represents the work required to bring the small ion from the surface of the macromolecule to an infinite distance (bulk solution).

Considering the conditional equilibrium constant for the overall dissociation reaction of the polyion, Eq.15,

$$K_a = \frac{[A^{Q-}][H^+]}{[AH^{(Q-1)-}]} = \frac{(A^{Q-})(H^+)}{(AH^{(Q-1)-})} \frac{\gamma_{Q-1}}{\gamma_Q \cdot \gamma_H} = K_{\text{int}} \frac{\gamma_{Q-1}}{\gamma_Q \cdot \gamma_H} \tag{18}$$

The ratio of polyion activity coefficients can be defined as an effective activity coefficient:[57]

$$\ln \gamma_{eff} = \ln \frac{\gamma_Q}{\gamma_{Q-1}} = -\frac{F\psi_0}{RT} \tag{19}$$

Hence, it is readily seen that this term represents a "local" ion activity correction for the proton (actually, a Boltzmann factor):

$$K_{\text{int}} = \frac{[A^{Q-}][H^+]}{[AH^{(Q-1)-}]} \gamma_{eff} \cdot \gamma_H = \frac{[A^{Q-}](H^+)_0}{[AH^{(Q-1)-}]} \tag{20}$$

where

$$(H^+)_0 = [H^+]\gamma_H \exp\left(-\frac{F\psi_0}{RT}\right) \tag{21}$$

The separate consideration of electrostatic and intrinsic energy contributions, Eq. 14, is the starting point of most treatments of the polyelectrolytic effects in macromolecules or biosorbents.

The value of ψ_0 is often estimated by solving the Poisson-Boltzmann equation,[58-60] which implies the description of the solid-liquid interface with a suitable model. By analogy with the models initially developed for humic and fulvic acids,[61] essentially, two groups of electrostatic models can be categorized differing in the structure of the biosorbent particles (Figure 2): ion-impermeable particles, in which the charge is placed on the surface, which have been employed for cadmium biosorption on bacterial surfaces,[62-64] and proton binding,[65] and ion-permeable particles considered as a gel into which ions can penetrate or Donnan models, which have been mainly used for interpreting biosorption data on marine algae.[66-72] Comparisons between different models including descriptions based in specific-ion interaction theory have also been carried out.[65, 67, 73]

If an appropriate electrostatic model is used, the dependence of the binding isotherms on ionic strength should vanish and the corrected isotherms will merge into a master curve,[74] which is independent of the electrolyte salt level. Briefly (see the scheme of Figure 3), the experimental proton titration data (a) can be transformed (through a charge balance) into a binding curve (b), which can be expressed as charge (Q), proton coverage (θ), dissociation degree, etc. versus pH. If the organic ligand is an acid (not amphoteric) substance, initially in its fully protonated form, then the proton release from the sample (in equilibrium with an electrolyte solution) will correspond to the absolute charge (Q), otherwise a correction term is required.[74] The set of charge curves obtained over a (preferably wide) range of ionic strengths (c) are used to optimize the parameters of the electrostatic model (Donnan volume, specific surface area, etc.). If the electric layer model is correct, the charge curves at different ionic strengths plotted versus pH_0, calculated from Eq. 21, yield a single master curve (d),

which can be used for the analysis of the intrinsic protonation parameters by means of an appropriate isotherm, obtaining the affinity spectrum (e), etc.

4. Kinetic studies

Equilibrium relationships comprise different conditions for biosorption process attributed to the necessary time for a system to achieve thermodynamic stability. Whereas biosorption extend is dependent only on the initial and final equilibrium states, the rate of biosorption is dependent on the way leading from the initial to the final step. Sorption solid-liquid kinetics may be controlled by several independent processes, which normally act in conjunction, involving transport phenomenon and chemical reactions. In porous media these include four steps:[75] transport of the sorbate (cadmium) in the bulk solution, film diffusion from the bulk solution through the boundary layer of fluid immediately adjacent to the external surface of the biosorbent particle, diffusion through the particle, and chemical binding reaction of the sorbate.

To properly understand adsorption kinetics, an accurate rate equation must be obtained for each step that takes place during the process. Thus, the overall kinetic model could be really difficult to evaluate. An useful approach to avoid this problem consists in identify the step or steps that limit the global rate of adsorption and then study them separately.

Normally, the transport process in the bulk solution and the film diffusion through the boundary layer of bioadsorbent are considered rapid processes, compared with pore intraparticle diffusion or sorption at internal surface sites. It is common to these rapid reactions to be sensitive to changes in experimental conditions that affect the rates of transport in solution, such as agitation, dispersion of the adsorbent, etc.[76] An adequate mixing, created by proper agitation, makes the transport of sorbate in solution to be neglected, which could contribute to suppress the boundary layer around the particles. Then, in most cases,

intraparticle diffusion or chemical binding reaction may control the sorption kinetic mechanism.

Moreover, if the mechanism cannot be confirmed when experimental sorption data are tested, system variables such as agitation speed, particle size, solute concentration, biosorbent mass and solution temperature should be extensively analysed.

4.1 Diffusion as rate controlling step

It is common to assume in biosorption that the overall rate of binding depends primarily on diffusivity of the sorbate. The effective intraparticle diffusivity and film diffusion coefficient are normally key parameters for prediction of sorption-desorption kinetics or process dynamic behaviour. Sorption isotherms are essential for the development of a mass transfer model. The use of non-linear isotherms (normally Langmuir model) in mass conservation equations makes impossible an analytical solution, while the introduction of linear isotherm equations clearly simplifies the solution process, although their application is really limited.[77]

One of the first used models to describe the diffusivities of metal ions in spherical adsorbents, allowing an exact mathematical solution for kinetics of the ion exchange process, was the shrinking core model (SCM).[78] It is based on the presence of an unreacted core of material surrounded by an outer layer of reacted material in a solid particle and it assumes that metal ions are rapidly and totally consumed at the core-shell interface. Due to its limitations, Seki and Suzuki [79] modified and adapted the SCM for the description of the rate process of cadmium and lead adsorption to a brown alga, considering that the metal ions can diffuse into the membranous adsorbent from two sides of flat slab. They obtained an average apparent diffusion coefficient for cadmium of about 9×10^{-6} $cm^2 \cdot s^{-1}$. Overall, diffusion process inside a porous particle is slower than in the corresponding homogeneous system, probably due to the combined effect of increased in tortuosity and charge density of polyelectrolyte which form

part of the biosorbent. As a result, the calculated diffusivity, or diffusion coefficient, inside the particles is an effective diffusivity which is smaller than the molecular diffusivity (7.2×10^{-6} $cm^2\cdot s^{-1}$ for cadmium at infinite dilution and 25 ºC)[80] in the absence of the sorbent material matrix.

Other models like the linear adsorption model (LAM), which assumes that equilibrium is developed between bound and unbound species at every point in the bed, have been employed to interpret the experimental kinetics of cadmium and other metals binding. This model is successfully used when the process being described is diffusion of a species along with reaction on internal surface or sites. Moreover, the bound metal concentration is considered a linear function of the free metal concentration; this restriction and the fact that external film diffusion may play a role, overall at the beginning of the process, make that the calculated cadmium intraparticle diffusion coefficients were very low ($5.8\text{-}48.3\times10^{-12}$ $cm^2\cdot s^{-1}$), compared to the cadmium effective diffusion coefficient, as it is showed in the work of Loukidou [8] for cadmium biosorption by *Aeromonas caviae*.

At the initial stage of metal ion sorption, the rate of the process is usually dominated by film diffusion rather than intraparticle diffusion because metal ion concentration inside the sorbent particle is very low. So that, the effect of film diffusion on the process rate cannot be neglected. In order to avoid this, Yang and Volesky [77] proposed a mathematical model for cadmium desorption process from formaldehyde *Sargassum f.* algae, and determined the cadmium intraparticle diffusivity at pH 2 and 1 (1.65 and around 3.7×10^{-6} $cm^2\cdot s^{-1}$, respectively). Later, these same authors [81] used a mass transfer model, assuming the intraparticle diffusion in a one-dimensional thin plate as a controlling step for cadmium biosorption by protonated *Sargassum f.* biomass, obtaining satisfactorily results. The diffusion coefficient of cadmium ion in the biomass regressed from the model at pH 4 was about 3.5×10^{-6} $cm^2\cdot s^{-1}$.

The effect of boundary layer resistance can also be modelled through inclusion of a mass transfer expression at the outside boundary. In this way, Evans et al. [82] used a pore diffusion model incorporating nonlinear adsorption to describe kinetic cadmium uptake data by chitosan-based crab shells, suggesting intraparticle diffusion as the rate limiting step. Choy et al. [83] analyzed the effect of external film boundary layer and intraparticle mass transfer resistance on the sorption process and its significance. They developed and tested four methods of determining the external film transport coefficient. The application of the intraparticle diffusion root time model demonstrated that intraparticle diffusion is the dominant mechanism for the sorption of cadmium onto bone char, except at the very beginning of the process for particle size between 500-700 μm of diameter; as particle size decreases the influence of the external film transport coefficient becomes much more significant.

The fact that the boundary layer around the particles is usually not completely suppressed with the increase in agitation rate is normally attributed to the fact that particles move at a comparable speed with the agitated liquid.

Recently, Vilar et al. [84] used a mass transfer model to simulate the cadmium concentration decrease over time and to predict the profile concentrations inside the *Gelidium* algae and agar extraction algal waste particles, either by the homogeneous diffusion model (HDM) or by the linear driving force model (that can be solved analytically), considering an average metal concentration inside the particle instead of a concentration profile as with the HDM. The obtained intraparticle homogeneous diffusion coefficient for cadmium ions is in the range of $0.05\text{-}2.2\times10^{-8}$ $cm^2 \cdot s^{-1}$.

In general, cadmium biosorption kinetics takes place in two stages: an initial rapid uptake during a few minutes attributed to a rapid surface adsorption, followed by a slower step that could correspond to interior particle penetration.[85] Due to the complicated

heterogeneous nature that the biosorbent materials usually present, cadmium binding mechanism is actually not clear and should be investigated further. Moreover, the assumptions employed for mass transfer model development, together with the difficult in determining some parameters present in the equations, can diminish the theoretical rigour of the model and affect the results.

4.2 Metal-biosorbent reaction as rate controlling step

Many attempts have been made to formulate a general expression describing the kinetics of chemisorption on heterogeneous surfaces. The models considering metal-biosorbent reaction as rate limiting step constitute a significant alternative to the diffusion equations considered above. In this case, metal diffusion, both in the bulk solution and in the biosorbent, is considered faster than the reaction that takes place in the active binding sites.

These models regard the biosorbent surface as a reactant and they suppose that the rate of the process is proportional to the quantity of available sites, applying the law of mass action. Moreover, it is assumed that all of the sites implicated in the binding are equivalent.[76]

The nature of the specific interactions between metal and adsorbent may influence the rate of the chemical binding reaction. As an example, physical adsorption processes are generally rapid (milliseconds or at most seconds), while chemical adsorption leads to slower rates. In this last case, bonds between metal and sites are formed and ruptured with larger activation energies involved, that produce a diminution in adsorption rate.[75]

The interactions that could take place in the biosorbent may involve different processes, such as reaction between metal and sites, formation and breaking of bounds, and reorganization of the biosorbent composition with appearance and loss of different species. These interactions, together with the well-known heterogeneity of biosorbents and the fact that transport phenomena and chemical reactions are normally complicated to be considered

as independent phenomena, make that simple rate empirical equations used for biosorption kinetics description were considered not adequate in some cases.[76]

The low knowledge of the biosorbents structure, appearance and behaviour makes impossible to distinguish between different kinetic models that describe the experimental kinetic data with identical accuracy, even if they are developed under diverse assumptions. Moreover, if a chemical rate expression is able to fit a given kinetic data, it cannot be supposed that the stoichiometric of the binding reaction is represented by the mentioned rate equation, so there is no correlation involving the applicability of these rate expressions and the nature of the biosorbent adsorption.

Nevertheless, the use of simple empirical expressions obtained from the law of mass action assuming certain mechanism, may describe with great accuracy any number of biosorption kinetics experiments. Thus, a chemical reaction could be the rate determining step in biosorption kinetics processes, although, there is no evidence to confirm this hypothesis.

Due to their simplicity and the reasonable representation of experimental data these models have been used by a great number of authors for the description of biosorption kinetics, although no consistent theoretical derivation can be found for these equations. Moreover, important kinetic parameters, such as the kinetic rate constant or the equilibrium sorption capacity, can be obtained.

Three of the most used simple empirical equations (Elovich, pseudo-first and pseudo-second equations), are worth mentioned following.

a) Elovich equation

The Elovich equation was initially proposed for the description of the kinetics of chemisorption of gases on solids. In this model, a variation in the energy of chemisorption is attributed to a change in the surface coverage or to a continuous and specific range of site reactivities.[86] The equation is formulated as:

$$\frac{dq_t}{dt} = a \cdot \exp(-b \cdot q_t) \tag{22}$$

It can also be represented in integrated form as:

$$q_t = \frac{1}{b} \cdot \ln(a \cdot b) + \frac{1}{b} \cdot \ln(t + t_0) \tag{23}$$

where a, b and t_0 =(1/a·b) are constants, and q_t represents the quantity adsorbed at any time, t. Parameter a gives an idea of the reaction rate constant, while b represents the rate of chemisorption at zero coverage. t_0 is an adjustable parameter that makes the plot linear over the entire range.

Only in few papers, Elovich equation has been successfully applied to solid adsorption in solution for the whole experimental kinetic data range, among them, the works of Cheung et al.,[87, 88] which study the cadmium adsorption kinetic using bone char. One must be aware of the limited conditions when this kind of integrated simple equations are used to fit a complex process. However, this equation can be effectively fitted at specific conditions for a certain data range, usually intermediate time data range.

b) Pseudo-first and pseudo-second order equations

These equations originally appear as an alternative for the Elovich model to describe adsorption kinetics of gases on solids.[89] As it was mentioned above, in many cases the Elovich equation is not able to describe the whole kinetic data range, and certain deviations from linearity are found, mainly attributed to kinetic mechanism changes. Therefore, simple empirical expressions, such as pseudo-first and pseudo-second order equations, based on the adsorption at vacant biosorbent surface sites, may be used if they are able to accuracy describe the complete kinetics experiences.

If it is assumed that adsorption rate only depends on the fraction of empty sites at time t, defining θ as the fraction of occupied sites, n as the number of sites occupied by each molecule of sorbate (metal) and k as the constant rate, the following equation can be obtained:

$$\frac{d\theta}{dt} = k \cdot (1-\theta)^n \tag{24}$$

Separating variables in Eq. 24 and integrating for $n \neq 1$ with the boundary conditions $\theta = 0$ for $t = 0$ and θ at time t, the following expression is obtained:

$$-\frac{1}{(1-\theta)^{n-1}} = (n-1) \cdot k \cdot t + 1 \tag{25}$$

or for $n=1$:

$$\theta = 1 - e^{-kt} \tag{26}$$

If this equation is rearranged, and the value for $\theta = q_t/Q_e$ (Q_e is the equilibrium sorption capacity) is introduced, the following equation is obtained:

$$\ln\frac{(Q_e - q_t)}{Q_e} = -k \cdot t \tag{27}$$

This equation represents the pseudo-first order equation, and it was originally proposed by Lagergren in 1898 based on solid capacity. The used of the prefix "pseudo-" implies that it is not a true first order kinetic rate expression.[76]

The pseudo-first order kinetic model is commonly used for the description of sorbate adsorption kinetics in many biosorption processes,[90-92] nevertheless the number of papers is reduced in the case of cadmium adsorption.[93, 94] It allows to obtain important kinetic parameters, describing experimental kinetic data with accuracy and in a simple manner. Therefore, if the plot of $\ln(Q_e-q_t)$ versus t gives a straight line with slope of k and intercept of $\ln(Q_e)$, the possibility of kinetic reaction rate control by a pseudo-first order model is suggested. However, in some cases this model is restricted to a partial portion of the reaction range and, besides, other available kinetic models have not been used to test and correlate the data.[95]

The pseudo-first order equation is the equivalent to the diffusion expression obtained for the cases of diffusion through a boundary liquid film, considering the linear driving force model.

On the other hand, if Eq. 25 is developed, the following expression can be obtained:

$$\frac{Q_e^{n-1}}{(Q_e - q_t)^{n-1}} = (n-1)\cdot k \cdot t + 1 \tag{28}$$

If n= 2 another equation based on biosorbent capacity can be obtained, that presents the following form:

$$\frac{1}{(Q_e - q_t)} = \frac{1}{Q_e} + \frac{k}{Q_e}\cdot t \qquad or \qquad \frac{t}{q_t} = \frac{1}{k\cdot Q_e} + \frac{1}{Q_e}\cdot t \tag{29}$$

In a similar way, Blanchard et al. [96] proposed a pseudo-second kinetic order equation with respect to the number of available binding sites (Q_e-q_t), obtaining an alternative differential equation to Eq. 24:

$$-\frac{dq_t}{dt} = k_2 \cdot (Q_e - q_t)^2 \tag{30}$$

Integration for the boundary conditions q_t= 0 at t= 0 and q_t at time t, gives:

$$\frac{1}{(Q_e - q_t)} = \frac{1}{Q_e} + k_2 \cdot t \qquad or \qquad q_t = \frac{Q_e^2 \cdot k_2 \cdot t}{1 + Q_e \cdot k_2 \cdot t} \tag{31}$$

The new kinetic constant, k_2, is the equivalent to k/Q_e term, obtained for the Ritchie's model (Eq. 29). Based on these equations, Ho [97] reported the linearized form of this pseudo-second order model, where sorbate removal from solution is due to purely physicochemical interactions between biosorbent and metal solution:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot Q_e^2} + \frac{1}{Q_e}\cdot t \tag{32}$$

From Ho´s work,[97] this experimental pseudo-second order model (equations 31 and 32) has been successfully applied to the description of many biosorption process in solution, including a great number of cadmium removal studies.[16, 90, 98-106] The great advantage of this

model over the other equations based on the reaction sorbate-biosorbent consists on its great accuracy in the description of the whole kinetic experimental data (Figure 4). Nevertheless, it must be taken into account that the fact that experimental data may be fitted by a rate equation is not sufficient evidence to consign the corresponding mechanism.

One of the greatest criticisms to these kinetics equations is the fact that they are approximations empirically deduced without a consistent theoretical derivation. This problem was recently solved in a general way by Azizian,[92] who derived an analytical solution for the pseudo-first and second order equations, and also determined the conditions for its application, identifying the real meaning of the observed rate coefficients as a complex function of initial concentration of solute. The general equation obtained by Azizian considering the adsorption and desorption of a solute in solution is represented by:

$$\frac{d\theta}{dt} = k_a \left(C_0 - \beta\theta\right)\cdot(1-\theta) - k_d\,\theta \qquad (33)$$

where k_a and k_d are the adsorption and desorption rate constants, respectively, θ is the surface coverage fraction and $\beta = (m\cdot Q_{max}\cdot V^{-1})$; Q_{max} represents the maximum biosorption capacity, m the mass of sorbent and V the solution volume.

If experimental conditions are such that the initial concentration of solute is very high compared to $\beta\cdot\theta$ ($C_0 >> \beta\cdot\theta$) then, this term can be ignored in Eq. 33 and as a result, the pseudo-first order equation is obtained (Eq. 27). In contrast, if the initial concentration of solute is not too high for the term $\beta\cdot\theta$ to be ignored, the pseudo-second order equation is obtained from the above general kinetic equation after several approximations.

It is interesting to note that the observed pseudo-first order kinetic constant is deduced to be a combination of the adsorption and desorption kinetic constants, as it is showed in Eq. 34. Therefore, the equilibrium constant ($K = k_a/k_d$) can be calculated from the linear function obtained if the k_1 values determined at different initial solute concentrations are plotted.

$$k_1 = k_a \cdot C_0 + k_d \tag{34}$$

On the other hand, in the deduction of the pseudo-second order equation, if the observed kinetic rate constant, k_2, is defined as in Eq. 35, the Ho´s linearized form model (Eq.32) is obtained, while if k_2 is defined as -γ/2, the more general equation proposed by Ritchie (Eq. 29) can be achieved.

$$k_2 = -\frac{\gamma}{2 \cdot Q_e} \tag{35}$$

The term γ is a complex function of initial solute concentration, adsorption-desorption constants and β (Eq. 36), so it is really difficult to relate the pseudo-second order kinetic constant to the initial solute concentration, obtaining a good correlation and an acceptable error for the different parameters.

$$k_2 = \frac{k_a \left[\sqrt{\left(\beta + C_0 + \frac{k_d}{k_a} \right)^2 - 4 C_0 \cdot \beta} \; + \; \left(\beta + C_0 + \frac{k_d}{k_a} \right) \right]}{2 Q_e} \tag{36}$$

Other equations, such as Langmuir or Freundlich type models, have been experimentally proposed to obtain the relation between the kinetic rate constant and the initial solute concentration or other experimental parameters.[103, 105, 107] The obtained results are satisfactory, although without theoretical rigour.

The only difference between the pseudo-second order equation proposed by Ritchie (Eq. 29) and those proposed by Blanchard (Eq. 31) or Ho (Eq. 32) is the value assigned to the kinetic rate constant obtained from data adjustment. However, only the model indicated by Blanchard and Ho, both the non-linearized and the linearized form of the pseudo-second order equation, can be applied to metal biosorption kinetic description, practically in all the cases.

In spite of everything, one must be aware that the effects of transport phenomena and chemical reactions are often experimentally inseparable.

5. CONCLUSIONS

It can be concluded that nowadays exists a wide amount of information about fundamental and basic aspects of the physical chemistry of the process of biosorption of cadmium in aqueous solutions.

In this review, this kind of information has been summarized from a methodological point of view into two great areas: thermodynamics and kinetics. Thermodynamic aspects considered, involves the study of the acid-base properties of the sorbent, the description of adsorption data in terms of isotherms and the consideration of electrostatic effects as a function of relevant variables, such as pH or ionic strength, associated to models of the biosorbent particle, as permeable or impermeable, to the electrolytic medium. Kinetic studies treat, essentially, the diffusion or the metal-biosorbent reaction as rate controlling steps, and different approaches are well-established.

All these kind of physicochemical studies constitute a previous and necessary step for further dynamic experiments in columns (papers about these important topics have been considered beyond the scope of this review) either in laboratory or in a pilot scale.

To summarize, it can be found below the main points that must be complete in this specified research field and the direction for the future development:

1.- To understand the acid-base and complexation properties of the different classes of biosorbents.

2.- To determine in all cases the electrostatic character of the sorbent particle and, consequently, to suggest an appropriate model for its behaviour in aqueous solution.

3.- To establish the kinetic equation for the biosorption process with a solid theoretical basis, as possible.

4.- To characterize the interaction of cadmium with different classes of biosorbents in the presence of other metals, in order to quantify competition effects either in batch or in columns.

5.- To transfer all basic knowledge about biosorption to the market. The application of basic information on cadmium biosorption, acquired along the last years, must be directly oriented to the solution of real environmental problems. This is the next challenge. So, researchers in this field must devote their efforts to that task sharing basic research with applications.

6. ACKNOWLEDGMENTS

The authors wish to thank Xunta de Galicia through project PGIDT02TAM10302PR, Ministerio de Ciencia y Tecnología through project BQU 2002-02133 and University of A Coruña for financial support.

7. REFERENCES

[1] *Official Journal of the European Union* **2006**, L33/1.

[2] C.P.C. Poon, in *Cadmium in the environment* (Eds Mislin H, Rivera O) **1986**, pp. 46 (Basel: Birkhaeuser)

[3] E. Percival, R.H. McDowell, *Chemistry and enzymology of marine algal polysaccharides* **1967,** (Academic Press:London New York).

[4] T.A. Davis, B. Volesky, A. Mucci, *Water Res.* **2003**, *37*, 4311.

[5] S. Klimmek, H.J. Stan, A. Wilke, G. Bunke, R. Buchholz, *Environ. Sci. Technol.* **2001**, *35*, 4283.

[6] Z.R. Holan, B. Volesky, I. Prasetyo, *Biotechnol. Bioeng.* **1993**, *41*, 819.

[7] A.I. Zouboulis, M.X. Loukidou, K.A. Matis, *Process Biochem.* **2004**, *39*, 909.

[8] M.X. Loukidou, T.D. Karapantsios, A.I. Zouboulis, K.A. Matis, *J. Chem. Technol. Biotechnol.* **2004**, *79*, 711.

[9] M.S. Dzul-Erosa, T.I. Saucedo-Medina, R. Navarro-Mendoza, M. Ávila-Rodríguez, E. Guibal, *Hydrometallurgy* **2001**, *61*, 157.

[10] B. Benguella, H. Benaissa, *Water Res.* **2002**, *36*, 2463.

[11] D. Mohan, C.U. Pittman Jr., P.H. Steele, *J. Colloid Interf. Sci.* **2006**, *297*, 489.

[12] W.S. Peternele, A.A. Winkler-Hechenleitner, E.A. Gómez-Pineda, *Bioresour. Technol.* **1999**, *68*, 95.

[13] H. Benaissa, *J. Hazard. Mater.* **2006**, *B132*, 189.

[14] R.P. Dhakal, K.N. Ghimire, K. Inoue, *Hydrometallurgy* **2005**, *79*, 182.

[15] M. Martínez, N. Miralles, S. Hidalgo, N. Fiol, I. Villaescusa, J. Poch, *J. Hazard. Mater.* **2006**, *B133*, 203.

[16] Z. Reddad, C. Gerente, Y. Andres, P. Le Cloirec, *Environ. Sci. Technol.* **2002**, *36*, 2067.

[17] U. Kumar, M. Bandyopadhyay, *Bioresour. Technol.* **2006**, *97*, 104.

[18] M.C. Basso, E.G. Cerrella, A.L. Cukierman, *Ind. Eng. Chem. Res.* **2002**, *41*, 3580.

[19] Y.S. Ho, C.C. Wang, *Process Biochem.* **2004**, *39*, 759.

[20] G. Crini, *Prog. Polym. Sci.* **2005**, *30*, 38.

[21] A. Demirbas, E. Pehlivan, F. Gode, T. Altun, G. Arslan, *J. Colloid Interf. Sci.* **2005**, *282*, 20.

[22] R. Leyva-Ramos, J.R. Rangel-Mendez, J. Mendoza-Barron, L. Fuentes-Rubio, R.M. Guerrero-Coronado, *Water Sci. Technol.* **1997**, *35*, 205.

[23] S.M. Dal Bosco, R. Sarti Jimenez, W. Alves Carvalho, *J. Colloid Interf. Sci.* **2005**, *281*, 424.

[24] O. Abollino, M. Aceto, M. Malandrino, C. Sarzanini, E. Mentasti, *Water Res.* **2003**, *37*, 1619.

[25] B. Volesky, Z.R. Holan, *Biotechnol. Prog.* **1995**, *11*, 235.

[26] F. Vegliò, F. Beolchini, *Hydrometallurgy* **1997**, *44*, 301.

[27] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, *Water Res.* **1999**, *33*, 2469.

[28] Y. Sag, *Separ. Purif. Method* **2001**, *30*, 1.

[29] S. Babel, T.A. Kurniawan, *J. Hazard. Mater.* **2003**, *B97*, 219.

[30] G. Crini, *Bioresour. Technol.* **2006**, *97*, 1061.

[31] J. Buffle, K.J. Wilkinson, S. Stoll, M. Filella, J. Zhang, *Environ. Sci. Technol.* **1998**, *32*, 2887.

[32] R. Herrero, B. Cordero, P. Lodeiro, C. Rey-Castro, M.E. Sastre de Vicente, *Mar. Chem.* **2006**, *99*, 106.

[33] A. Katchalsky, P. Spitnik, *J. Polym. Sci.* **1947**, *2*, 432.

[34] R.H. Crist, J.R. Martin, P.W. Guptill, J.M. Eslinger, D.R. Crist, *Environ. Sci. Technol.* **1990**, *24*, 337.

[35] R.H. Crist, K. Oberholser, J. McGarrity, D.R. Crist, J.K. Johnson, J.M. Brittsan, *Environ. Sci. Technol.* **1992**, *26*, 496.

[36] D.R. Crist, R.H. Crist, J.R. Martin, J.R. Watson, *FEMS Mibrobiology Reviews* **1994**, *14*, 309.

[37] R.H. Crist, J.R. Martin, D.R. Crist, *Environ. Sci. Technol.* **1999**, *33*, 2252.

[38] R.H. Crist, J.R. Martin, D.R. Crist, *Environ. Sci. Technol.* **2002**, *36*, 1485.

[39] K.Y.H. Gin, Y.Z. Tang, M.A. Aziz, *Water Res.* **2002**, *36*, 1313.

[40] S. Schiewer, B. Volesky, *Environ. Sci. Technol.* **1996**, *30*, 2921.

[41] F. Pagnanelli, S. Mainelli, S. De Angelis, L. Toro, *Water Res.* **2005**, *39*, 1639.

[42] P. Lodeiro, C. Rey-Castro, J.L. Barriada, M.E. Sastre de Vicente, R. Herrero, *J. Colloid Interf. Sci.* **2005**, *289*, 352.

[43] S. Schiewer, M.H. Wong, *Environ. Sci. Technol.* **1999**, *33*, 3821.

[44] R.H. Crist, J.R. Martin, D. Carr, J.R. Watson, H.J. Clarke, D.R. Crist, *Environ. Sci. Technol.* **1994**, *28*, 1859.

[45] R.H. Crist, J.R. Martin, J. Chonko, D.R. Crist, *Environ. Sci. Technol.* **1996**, *30*, 2456.

[46] S. Schiewer, B. Volesky, *Environ. Sci. Technol.* **1995**, *29*, 3049.

[47] Y.S. Yun, B. Volesky, *Environ. Sci. Technol.* **2003**, *37*, 3601.

[48] P. Miretzky, A. Saralegui, A. Fernández Cirelli, *Chemosphere* **2006**, *62*, 247.

[49] I.A.H. Schneider, J. Rubio, R.W. Smith, *Int. J. Miner. Pross.* **2001**, *62*, 111.

[50] D.G. Kinniburgh, W.H. van Riemsdijk, L.K. Koopal, M. Borkovec, M.F. Benedetti, M.J. Avena, *Colloid Surface A* **1999**, *151*, 147.

[51] L.K. Koopal, T. Saito, J.P. Pinheiro, W.H. Van Riemsdijk, *Colloid Surface A* **2005**, *265*, 40.

[52] F. Pagnanelli, S. Mainelli, L. Toro, *Hydrometallurgy* **2005**, *80*, 107.

[53] C. Lamelas, F. Avaltroni, M.F. Benedetti, K.J. Wilkinson, V.I. Slaveykova, *Biomacromol.* **2005**, *6*, 2756.

[54] X.S. Li, P. Englezos, *J. Colloid Interf. Sci.* **2005**, *281*, 267.

[55] M.E. Sastre de Vicente, *Curr. Top. Solution Chem.* **1997**, *2*, 157.

[56] C. Tanford, *Physical Chemistry of macromolecules* **1961,** (John Wiley & Sons, Inc.).

[57] F. Morel, J.G. Hering, *Principles and applications of aquatic chemistry* **1993,** (Wiley:New York).

[58] M. Borkovec, B. Jönsson, G.J.M. Koper, *Surface and colloid science* **2001**, *16*, 99.

[59] B.M. Bartschat, S.E. Cabaniss, F.M.M. Morel, *Environ. Sci. Technol.* **1992**, *26*, 284.

[60] J.C.M. de Wit, W.H. Van Riemsdijk, L.K. Koopal, *Environ. Sci. Technol.* **1993**, *27*, 2005.

[61] T. Saito, S. Nagasaki, S. Tanaka, L.K. Koopal, *Colloid Surface A* **2005**, *265*, 104.

[62] Z. Reddad, C. Gerente, Y. Andres, P. Le Cloirec, *Environ. Sci. Technol.* **2002**, *36*, 2242.

[63] D.M. Borrok, J.B. Fein, *J. Colloid Interf. Sci.* **2005**, *286*, 110.

[64] N. Yee, J. Fein, *Geochim. Cosmochim. Acta* **2001**, *65*, 2037.

[65] C. Rey-Castro, R. Herrero, M.E. Sastre de Vicente, *Chem. Spec. Bioavail.* **2004**, *16*, 61.

[66] C. Rey-Castro, P. Lodeiro, R. Herrero, M.E. Sastre de Vicente, *Environ. Sci. Technol.* **2003**, *37*, 5159.

[67] C. Rey-Castro, R. Herrero, M.E. Sastre de Vicente, *J. Electroanal. Chem.* **2004**, *564*, 223.

[68] F. Pagnanelli, F. Vegliò, L. Toro, *Chemosphere* **2004**, *54*, 905.

[69] S. Schiewer, *J. Appl. Phycol.* **1999**, *11*, 79.

[70] S. Schiewer, M.H. Wong, *Chemosphere* **2000**, *41*, 271.

[71] S. Schiewer, B. Volesky, *Environ. Sci. Technol.* **1997**, *31*, 1863.

[72] S. Schiewer, B. Volesky, *Environ. Sci. Technol.* **1997**, *31*, 2478.

[73] C. De Stefano, A. Gianguzza, D. Piazzese, S. Sammartano, *Anal. Bioanal. Chem.* **2005**, *383*, 587.

[74] J.C.M. de Wit, W.H. Van Riemsdijk, M.M. Nederlof, D.G. Kinniburgh, L.K. Koopal, *Anal. Chim. Acta* **1990**, *232*, 189.

[75] W.J. Weber Jr., P.M. McGinley, L.E. Katz, *Water Res.* **1991**, *25*, 499.

[76] C. Aharoni, D.L. Sparks, in *Rates of soil chemical processes* (Eds Sparks DL, Suárez DL) **1991**, pp. 1 (Soil Science Society of America: Madison (WI))

[77] J. Yang, B. Volesky, *J. Chem. Technol. Biotechnol.* **1996**, *66*, 355.

[78] D. Chen, Z. Lewandowski, F. Roe, P. Surapaneni, *Biotechnol. Bioeng.* **1993**, *41*, 755.

[79] H. Seki, A. Suzuki, *J. Colloid Interf. Sci.* **2002**, *246*, 259.

[80] J. Heyrovsky, J. Kuta, *Principles of polarography* **1966,** (Pub. House of Czechoslovak Academy of Sciences;
Academic Press:Prague,
New York,).

[81] J. Yang, B. Volesky, *Environ. Sci. Technol.* **1999**, *33*, 751.

[82] J.R. Evans, W.G. Davids, J.D. MacRae, A. Amirbahman, *Water Res.* **2002**, *36*, 3219.

[83] K.K.H. Choy, D.C.K. Ko, C.W. Cheung, J.F. Porter, G. McKay, *J. Colloid Interf. Sci.* **2004**, *271*, 284.

[84] V.J.P. Vilar, C.M.S. Botelho, R.A.R. Boaventura, *Water Res.* **2006**, *40*, 291.

[85] P. Brassard, E. Macedo, S. Fish, *Environ. Sci. Technol.* **1996**, *30*, 3216.

[86] H. Teng, C.T. Hsieh, *Industrial & Engineering Chemistry Research* **1999**, *38*, 292.

[87] C.W. Cheung, J.F. Porter, G. McKay, *J. Chem. Technol. Biotechnol.* **2000**, *75*, 963.

[88] C.W. Cheung, J.F. Porter, G. McKay, *Water Res.* **2001**, *35*, 605.

[89] A.G. Ritchie, *J. Chem. Soc., Faraday Trans.* **1977**, *33*, 1650.

[90] Y.S. Ho, G. McKay, *Process Biochem.* **1999**, *34*, 451.

[91] K.H. Chu, M.A. Hashim, *J. Chem. Technol. Biotechnol.* **2002**, *77*, 685.

[92] S. Azizian, *J. Colloid Interf. Sci.* **2004**, *276*, 47.

[93] Y. Liu, S.F. Yang, H. Xu, L.H. Woon, Y.M. Lin, J.H. Tay, *Process Biochem.* **2003**, *38*, 997.

[94] A. Benhammou, A. Yaacoubi, L. Nibou, B. Tanouti, *J. Colloid Interf. Sci.* **2005**, *282*, 320.

[95] Y.S. Ho, G. McKay, *Trans IChemE* **1998**, *76B*, 332.

[96] G. Blanchard, M. Maunaye, G. Martin, *Water Res.* **1984**, *18*, 1501.

[97] Y.S. Ho, D.A.J. Wase, C.F. Forster, *Environ. Technol.* **1996**, *17*, 71.

[98] V.C. Taty-Costodes, H. Fauduet, C. Porte, A. Delacroix, *J. Hazard. Mater.* **2003**, *B105*, 121.

[99] M. Horsfall Jr., A.A. Abia, A.I. Spiff, *Bioresour. Technol.* **2006**, *97*, 283.

[100] M.Y. Arica, Y. Kaçar, Ö. Genç, *Bioresour. Technol.* **2001**, *80*, 121.

[101] Z. Aksu, *Sep. Purif. Technol.* **2001**, *21*, 285.

[102] P. Vasudevan, V. Padmavathy, S.C. Dhingra, *Bioresour. Technol.* **2003**, *89*, 281.

[103] P. Lodeiro, B. Cordero, Z. Grille, R. Herrero, M.E. Sastre de Vicente, *Biotechnol. Bioeng.* **2004**, *88*, 237.

[104] P. Lodeiro, J.L. Barriada, R. Herrero, M.E. Sastre de Vicente, *Environ. Pollut.* **2006**, *142*, 264.

[105] B. Cordero, P. Lodeiro, R. Herrero, M.E. Sastre de Vicente, *Environ. Chem.* **2004**, *1*, 180.

[106] P. Lodeiro, B. Cordero, J.L. Barriada, R. Herrero, M.E. Sastre de Vicente, *Bioresour. Technol.* **2005**, *96*, 1796.

[107] Y.S. Ho, G. McKay, *Trans IChemE* **1999**, *77B*, 165.

[108] K. Chojnacka, A. Chojnacki, H. Górecka, *Chemosphere* **2005**, *59*, 75.

[109] A. Sharma, K.G. Bhattacharyya, *J. Hazard. Mater.* **2005**, *B125*, 102.

[110] P. Yin, Q. Yu, Z. Lin, P. Kaewsarn, *Environ. Technol.* **2001**, *22*, 509.

[111] H.S. Lee, J.H. Suh, I.B. Kim, T. Yoon, *Miner. Eng.* **2004**, *17*, 487.

[112] Y. Yalçinkaya, L. Soysal, A. Denizli, M.Y. Arica, S. Bektas, Ö. Genç, *Hydrometallurgy* **2002**, *63*, 31.

[113] Q. Yu, J.T. Matheickal, P. Yin, P. Kaewsarn, *Water Res.* **1999**, *33*, 1534.

[114] J.T. Matheickal, Q. Yu, G.M. Woodburn, *Water Res.* **1999**, *33*, 335.

[115] J. Rincón, F. González, A. Ballester, M.L. Blázquez, J.A. Muñoz, *J. Chem. Technol. Biotechnol.* **2005**, *80*, 1403.

[116] M. Iqbal, R.G.J. Edyvean, *Biotechnol. Lett.* **2004**, *26*, 165.

[117] C.C.V. Cruz, A.C.A. Costa, C.A. Henriques, A.S. Luna, *Bioresour. Technol.* **2004**, *91*, 249.

[118] A. Leusch, Z.R. Holan, B. Volesky, *J. Chem. Technol. Biotechnol.* **1995**, *62*, 279.

[119] M. Khosravi, R. Rakhshaee, M. Taghi Ganji, *J. Hazard. Mater.* **2005**, *B127*, 228.

[120] H.K. An, B.Y. Park, D.S. Kim, *Water Res.* **2001**, *35*, 3551.

[121] A. Leusch, Z.R. Holan, B. Volesky, *Appl. Biochem. Biotechnol.* **1996**, *61*, 231.

[122] S. Srikrajib, A. Tongta, P. Thiravetyan, K. Sivaborvorn, in *Biohydrometallurgy and the environment toward the mining of the 21st century* (Eds Amils R, Ballester A) **1999**, pp. (Elsevier:

[123] T.Y. Hsien, G.L. Rorrer, *Ind. Eng. Chem. Res.* **1997**, *36*, 3631.

[124] Y. Suzuki, T. Kametani, T. Maruyama, *Water Res.* **2005**, *39*, 1803.

[125] T.A. Davis, B. Volesky, R.H.S.F. Vieira, *Water Res.* **2000**, *34*, 4270.

[126] M. Iqbal, R.G.J. Edyvean, *Chemosphere* **2005**, *61*, 510.

[127] P.X. Sheng, Y.P. Ting, J.P. Chen, L. Hong, *J. Colloid Interf. Sci.* **2004**, *275*, 131.

[128] K.H. Chong, B. Volesky, *Biotechnol. Bioeng.* **1995**, *47*, 451.

[129] D. Feng, C. Aldrich, *Hydrometallurgy* **2004**, *73*, 1.

[130] M.A. Hashim, K.H. Chu, *Chem. Eng. J.* **2004**, *97*, 249.

[131] N. Lázaro, A. López Sevilla, S. Morales, A.M. Marqués, *Water Res.* **2003**, *37*, 2118.

[132] D. Zhou, L. Zhang, J. Zhou, S. Guo, *Water Res.* **2004**, *38*, 2643.

[133] A. Selatnia, M.Z. Bakhti, A. Madani, L. Kertous, Y. Mansouri, *Hydrometallurgy* **2004**, *75*, 11.

[134] P. Yin, Q. Yu, B. Jin, Z. Ling, *Water Res.* **1999**, *33*, 1960.

[135] I.A. Schneider, J. Rubio, *Environ. Sci. Technol.* **1999**, *33*, 2213.

[136] A.H. Hawari, C.N. Mulligan, *Bioresour. Technol.* **2006**, *97*, 692.

[137] C.W. Cheung, C.K. Chan, J.F. Porter, G. McKay, *Environ. Sci. Technol.* **2001**, *35*, 1511.

[138] G. Ozdemir, N. Ceyhan, T. Ozturk, F. Akirmak, T. Cosar, *Chem. Eng. J.* **2004**, *102*, 249.

[139] J.S. Chang, R. Law, C.C. Chang, *Water Res.* **1997**, *31*, 1651.

[140] S. Chamarthy, C.W. Seo, W.E. Marshall, *J. Chem. Technol. Biotechnol.* **2001**, *76*, 593.

[141] Z.R. Holan, B. Volesky, *Appl. Biochem. Biotechnol.* **1995**, *53*, 133.

[142] R. Leyva-Ramos, L.A. Bernal-Jacome, I. Acosta-Rodríguez, *Sep. Purif. Technol.* **2005**, *45*, 41.

[143] K.K.H. Choy, G. McKay, *Chemosphere* **2005**, *60*, 1141.

[144] D.C.K. Ko, C.W. Cheung, K.K.H. Choy, J.F. Porter, G. McKay, *Chemosphere* **2004**, *54*, 273.

[145] A. Özer, D. Özer, H.I. Ekiz, *Process Biochem.* **1999**, *34*, 919.

[146] A.A. Abia, M. Harsfall Jr., O. Didi, *Bioresour. Technol.* **2003**, *90*, 345.

[147] A. Esposito, F. Pagnanelli, A. Lodi, C. Solisio, F. Vegliò, *Hydrometallurgy* **2001**, *60*, 129.

[148] E. Fourest, C. Canal, J.-C. Roux, *FEMS Mibrobiology Reviews* **1994**, *14*, 325.

[149] S.J. Allen, P.A. Brown, *J. Chem. Technol. Biotechnol.* **1995**, *62*, 17.

[150] M. Ghoul, M. Bacquet, M. Morcellet, *Water Res.* **2003**, *37*, 729.

[151] K.C. Justi, V.T. Fávere, M.C.M. Laranjeira, A. Neves, R.A. Peralta, *J. Colloid Interf. Sci.* **2005**, *291*, 369.

[152] D. Mohan, K.P. Singh, *Water Res.* **2002**, *36*, 2304.

[153] G.D. Matos, M.A.Z. Arruda, *Process Biochem.* **2003**, *39*, 81.

[154] Y. Göksungur, S. Üren, U. Güvenç, *Bioresour. Technol.* **2005**, *96*, 103.

[155] S.S. Gupta, K.G. Bhattacharyya, *J. Hazard. Mater.* **2006**, *B128*, 247.

[156] F. Saiano, M. Ciofalo, S.O. Cacciola, S. Ramirez, *Water Res.* **2005**, *39*, 2273.

[157] R.J.E. Martins, R. Pardo, R.A.R. Boaventura, *Water Res.* **2004**, *38*, 693.

[158] E. Fourest, J.C. Roux, *Appl. Microbiol. Biotechnol.* **1992**, *37*, 399.

[159] F. Pagnanelli, A. Esposito, F. Vegliò, *Water Res.* **2002**, *36*, 4095.

[160] G. McKay, J.F. Porter, *J. Chem. Technol. Biotechnol.* **1997**, *69*, 309.

[161] G. Yan, T. Viraraghavan, *Water Res.* **2003**, *37*, 4486.

[162] M.M. Rao, A. Ramesh, G.P.C. Rao, K. Seshaiah, *J. Hazard. Mater.* **2006**, *B129*, 123.

[163] K.S. Low, C.K. Lee, S.C. Liew, *Process Biochem.* **2000**, *36*, 59.

[164] A. Saeed, M.W. Akhter, M. Iqbal, *Sep. Purif. Technol.* **2005**, *45*, 25.

[165] B. Benguella, H. Benaissa, *Colloid Surface A* **2002**, *201*, 143.

[166] F. Pagnanelli, M. Petrangeli Papini, L. Toro, M. Trifoni, F. Vegliò, *Environ. Sci. Technol.* **2000**, *34*, 2773.

[167] V.K. Gupta, S. Sharma, *Environ. Sci. Technol.* **2002**, *26*, 3612.

[168] M.I. Martín, F.A. López, C. Pérez, A. López-Delgado, F.J. Alguacil, *J. Chem. Technol. Biotechnol.* **2005**, *80*, 1223.

[169] R. Pardo, M. Herguedas, E. Barrado, M. Vega, *Anal. Bioanal. Chem.* **2003**, *376*, 26.

[170] J. Shen, Z. Duvnjak, *Process Biochem.* **2005**, *40*, 3446.

[171] F. Pagnanelli, S. Mainelli, F. Vegliò, L. Toro, *Chem. Eng. Sci.* **2003**, *58*, 4709.

[172] T. Gotoh, K. Matsushima, K.I. Kikuchi, *Chemosphere* **2004**, *55*, 135.

[173] V.K. Gupta, C.K. Jain, I. Ali, M. Sharma, V.K. Saini, *Water Res.* **2003**, *37*, 4038.

[174] K.K. Singh, A.K. Singh, S.H. Hasan, *Bioresour. Technol.* **2006**, *97*, 994.

[175] M.J. Avena, L.K. Koopal, W.H. van Riemsdijk, *J. Colloid Interf. Sci.* **1999**, *217*, 37.

Table 1

Maximum cadmium adsorption values obtained from different materials.

Adsorbent	$Q_{max,Cd}$ (mmol·g^{-1})	$Q_{max,Cd}$ (mg·g^{-1})	Ref
Lyngbya taylorii-phosphorylated	2.52	283.2	[5]
Ascophyllum nodosum	1.91	215	[6]
Bacillus laterosporus	1.42	159.5	[7]
Spirulina sp. (blue-green algae)	1.41	159	[108]
Neem (*Azadirachta indica*) leaf powder	1.4	157.8	[109]
Aeromonas caviae	1.38	155.3	[8]
Laminaria japonica	1.35	151.7	[110]
Chitosan	1.33	150	[9]
Broad bean peel	1.31	147.7	[13]
Bacillus licheniformis	1.27	142.7	[7]
Kraft lignin	1.22	137.1	[11]
Laminaria japonica	1.21	136	[111]
Trametes versicolor (immobilized onto carboxymethylcellulose beads)	1.2	134.5	[112]
Durvillaea potatorum	1.18	132.6	[113]
Sargassum natans	1.17	132	[6]
Lessonia flavicans	1.16	130.4	[113]
Ecklonia maxima	1.15	129.3	[113]
Durvillaea potatorum ($CaCl_2$ pretr.)	1.12	125.9	[114]
Fucus vesiculosus	1.12	125.9	[115]

Laminaria japonica	1.11	124.8	[113]
Orange waste	1.1	123.6	[14]
Lessonia nigresense	1.1	123.6	[113]
Alginate coated loofa sponge discs	1.09	122	[116]
Trametes versicolor Ca-alginates	1.07	120.6	[100]
Sargassum sp.	1.07	120	[117]
Sargassum fluitans Glutaraldehyde crss.	1.07	120	[118]
Peas peel	1.06	118.9	[13]
Ecklonia radiata	1.04	116.9	[113]
Ascophyllum nodosum	1.03	115.8	[113]
Pretreated *Azolla filiculoides* (water fern)	0.992	111.5	[119]
Crab shell (*Chinonecetes opilio*)	0.99	111.3	[120]
Sargassum fluitans (stipes)	0.99	111	[121]
Chlorella vulgaris	0.988	111.1	[101]
Sargassum fluitans PEI crosslinked	0.97	109	[118]
Sargassum fluitans (native)	0.96	108	[121]
Ascophyllum nodosum (native)	0.96	108	[121]
Sargassum fluitans Formaldehyde crss.	0.95	107	[118]
Fig leaves	0.92	103.1	[13]
Sargassum fluitans (blades)	0.92	103	[121]
Fucus vesiculosus (HCl pretr.)	0.92	103.4	[115]
Sargassum polycystum	0.92	103.36	[122]
Amberlite IR-120	0.899	101	[21]
Scolecite (zeolite)	0.89	100	[23]

Chitosan gel beads cross. GA	0.89	100	[123]
Sargassum muticum Formaldehyde crss.	0.88	99	[103]
Medlar peel	0.87	98.1	[13]
Ascophyllum nodosum PEI crss.	0.87	98	[118]
Ascophyllum nodosum Formaldehyde crss.	0.85	96	[118]
Sargassum muticum protonated	0.85	95	[103]
Saccorhiza polyschides	0.85	95	[106]
Laminaria hyperbola	0.82	92.2	[113]
Ulva onoi (alkali-pretr.)	0.807	90.7	[124]
Sargassum vulgare	0.79	88.9	[125]
Fucus vesiculosus	0.79	88.8	[32]
Phanerochaete chrysosporium (immobilized biomass on loofa sponge disk)	0.79	89	[126]
Sargassum muticum (acetone pretreatment)	0.78	88	[103]
Sargassum muticum (methanol pretre.)	0.77	86	[103]
Sargassum muticum (KOH pretr.)	0.77	86	[103]
Fucus vesiculosus ($CaCl_2$ pretr.)	0.76	85.4	[115]
Sargassum sp.	0.76	85.4	[127]
Ascophyllum nodosum	0.75	84.3	[128]
Padina sp.	0.75	84.3	[127]
Ecklonia maxima	0.74	83.5	[129]
Sargassum baccularia (brown)	0.74	83.2	[130]
Sargassum siliquosum (brown)	0.73	82.1	[130]
Calcium alginate beads	0.73	82	[116]

Fucus serratus	0.72	80.9	[32]
Sargassum fluitans	0.71	79.8	[125]
Ascophyllum nodosum	0.7	79	[106]
Sargassum muticum	0.68	76.4	[125]
Pelvetia caniculata	0.67	75	[106]
Sargassum filipendula	0.66	74.2	[125]
Phanerochaete chrysosporium (free)	0.66	74	[126]
Bifurcaria bifurcata	0.66	74	[106]
Fucus ceranoides	0.65	73.1	[32]
Fucus vesiculosus	0.65	73	[6]
Gellan gum gel beads	0.62	69.7	[131]
Cellulose/chitin beads	0.62	69.7	[132]
Carboxymethylated lignin	0.602	67.7	[12]
Sargassum muticum	0.58	65	[103]
Fucus vesiculosus (Formaldehyde pretr.)	0.58	65.1	[115]
Ulva sp.	0.58	65.2	[127]
Fucus spiralis	0.57	64	[105]
Laminaria ochroleuca	0.57	64	[106]
Streptomyces rimosus (NaOH pretr.)	0.56	63.3	[133]
Rhizopus arrhizus (pretreated)	0.56	62.9	[134]
Ulva onoi (non treated)	0.551	61.9	[124]
Potamogenon lucens (macrophytes)	0.55	61.4	[135]
Potamogenon lucens	0.55	61.4	[135]
Sargassum muticum ($Ca(OH)_2$ pretr.)	0.54	61	[103]

Padina tetrastomatica (brown)	0.53	59.6	[130]
Anaerobic granular sludge	0.53	60	[136]
Bone char	0.52	58.5	[137]
Pantoea sp. TEM18 (gram negative bact.)	0.52	58.1	[138]
Pseudomonas aeruginosa	0.51	57.4	[139]
Sargassum muticum ($CaCl_2$ pretr.)	0.51	57	[103]
Modified peanut shells	0.5	56.2	[140]
Duolite GT-73	0.5	56	[6]
Penicillium chrysogenum	0.5	56	[141]
Spruce sawdust-phosphorylated	0.5	56	[141]
Corncob (oxidized)	0.5	55.7	[142]
Chaetomorpha linum (green)	0.48	53.9	[130]
Bone char	0.477	53.6	[143]
Bone char	0.477	53.6	[144]
Ascophyllum nodosum Glutaraldehyde crss	0.46	52	[118]
Schizomeris leibleinii (green alga)	0.44	49.25	[145]
Rhizopus arrhizus (fresh)	0.4	45	[134]
Thiolated cassava waste	0.39	44.8	[146]
Sphaerotilus natans	0.39	43.8	[147]
Rhizopus arrhizus	0.39	43.8	[148]
Ulva onoi (acid-pretr.)	0.383	43	[124]
Rhizopus arrhizus (dry)	0.38	42.7	[134]
Aspergillus oryzae (pretreated)	0.38	42.7	[134]
Lyngbya taylorii	0.37	41.6	[5]

Rhizopus oligosporus (pretreated)	0.37	41.6	[134]
Lignite	0.358	40.3	[149]
PEI-silica gel	0.34	38.5	[150]
Chemically modified chitosan	0.34	38.5	[151]
Activated carbon from bagasse	0.34	38.03	[152]
Rhizopus oryzae (pretreated)	0.31	34.8	[134]
Chlorella vulgaris	0.3	33.7	[5]
Gracillaria sp.	0.3	33.7	[127]
Vermicompost	0.29	33.01	[153]
Ethanol treated baker´s yeast	0.28	31.7	[154]
Rhizopus orchidis	0.28	31	[141]
Montmorillonite	0.27	30.7	[155]
Rhizopus arrhizus	0.27	30	[141]
Coralline algae (red marine alga)	0.26	29.7	[18]
Stevensite	0.26	28.9	[94]
Phomopsis sp. biomaterial	0.26	29.2	[156]
Carboxymethylcellulose	0.26	28.7	[112]
Grape stalk waste	0.25	27.9	[15]
Fontinalis antipyretica (moss)	0.25	28	[157]
Rhizopus arrhizus	0.24	26.8	[158]
Gracilaria edulis (red)	0.24	27	[130]
Gracilaria changii (red)	0.23	25.9	[130]
R.nigricans crosslinked 1-Cl-2,3-epoxypropane	0.23	26	[141]
Sphaerotilus natans	0.228	25.6	[159]

Sugar beet pulp	0.217	24.4	[16]
Peat	0.188	21.1	[160]
Rice husk (NaOH treated)	0.18	20.24	[17]
Mucor ruoxii (fungus)	0.18	20.31	[161]
Brazil nutshells	0.17	19.4	[18]
Rhizopus nigricans	0.17	19	[141]
Ceiba pentandra hulls Activated carbon	0.17	19.5	[162]
Sawdust of *Pinus sylvestris*	0.17	19.1	[98]
Gracilaria salicornia (red)	0.16	18	[130]
Gelidium sesquipedale (red alga)	0.16	18	[84]
Tree fern	0.15	16.3	[19]
Spent grain	0.15	17.3	[163]
Papaya wood	0.15	17.22	[164]
Rice husk ($NaHCO_3$ treated)	0.144	16.18	[17]
Chitin	0.14	16.18	[165]
Cassava waste	0.13	14.3	[146]
Arthrobacter sp.	0.119	13.4	[166]
Red mud	0.116	13	[167]
Rice husk (epichlorohydrin treated)	0.099	11.12	[17]
Sugarcane bagasse	0.096	10.7	[18]
Agar extraction algal waste	0.096	9.7	[84]
Blast furnace sludge (80ºC)	0.09	10.15	[168]
Rice husk	0.076	8.58	[17]
Activated carbon (25º pH 7)	0.074	8.32	[22]

Pseudomonas putida	0.071	8	[169]
Corncob particles	0.07	7.9	[170]
Prosopis ruscifolia sawdust	0.066	7.4	[18]
Olive pomace	0.062	7	[171]
Kaolinite	0.06	6.8	[155]
Blast furnace sludge (20ºC)	0.06	6.74	[168]
Alginate-Chitosan hybrid beads	0.059	6.63	[172]
Na-Montmorillonite	0.05	5.2	[24]
Stems of Arundo donax	0.05	5.7	[18]
Corncob (natural)	0.048	5.38	[142]
Pistia stratiotes (macrophytes)	0.037	4.16	[48]
Spirodela intermedia (macrophytes)	0.036	4.04	[48]
Lemna minor (macrophytes)	0.033	3.71	[48]
Bagasse fly ash	0.018	2	[173]
Rolling mill scale (80ºC)	0.01	1.2	[168]
Wheat bran	0.006	0.7	[174]
Rolling mill scale (20ºC)	0.00098	0.11	[168]

Table 2

Adsorption isotherm equations.

Isotherm	Equation	Adjustable parameters
Langmuir	$Q = \frac{Q_{\max} \cdot b \cdot C}{1 + b \cdot C}$	2
Freundlich	$Q = K_f \cdot C^{1/n}$	2
Langmuir-Freundlich	$Q = \frac{Q_{\max} \cdot (b \cdot C)^{1/n}}{1 + (b \cdot C)^{1/n}}$	3
Tóth	$Q = \frac{Q_{\max} \cdot b \cdot C}{\left[1 + (b \cdot C)^{1/n}\right]^n}$	3

Figure captions

Figure 1:

a) Proton binding by *F. serratus* (in absence of cadmium) in 0.05 M $NaNO_3$ (from Herrero et al. [32]). Symbols represent experimental points (two replicate experiments are shown), solid line corresponds to the best fit of a Langmuir-Freundlich isotherm, Eq. 13, and dotted line to a simple Langmuir isotherm, equivalent to Eq. 13 with m_H =1. In both cases, the value of $Q_{max,H}$ was set equal to the total amount of titratable groups, determined from the equivalence point of the base titrations.

b) Cadmium binding by *F. serratus* at different pH values in 0.05 M $NaNO_3$ (from Herrero et al.[32]). Points are experimental points (mean values), solid lines are the fitted NICA isotherms (Eq. 10) and dotted lines represent fitted ideal competitive Langmuir isotherms, Eq. 9, (assuming 1:1 stoichiometry) using the parameters determined in proton binding fit (a).

Figure 2: Schematic representation of the impermeable sphere (a) and Donnan (b) models. Adapted from the article of Avena et al. [175]

Figure 3: Schematic representation of the procedure for the analysis of proton tritation data (adapted from de Wit el al.,[74] using experimental data from Rey-Castro et al. [66])

Figure 4: Kinetics of cadmium uptake by *Fucus spiralis* at several solution pH values (from Cordero et al.[105] Lines represent modelled results using the pseudo-second order model, Equation (31), at temperature of 25 ± 0.1 ºC, initial cadmium concentration 250 $mg \cdot L^{-1}$ and alga dose 2.5 $g \cdot L^{-1}$.

Figure 1

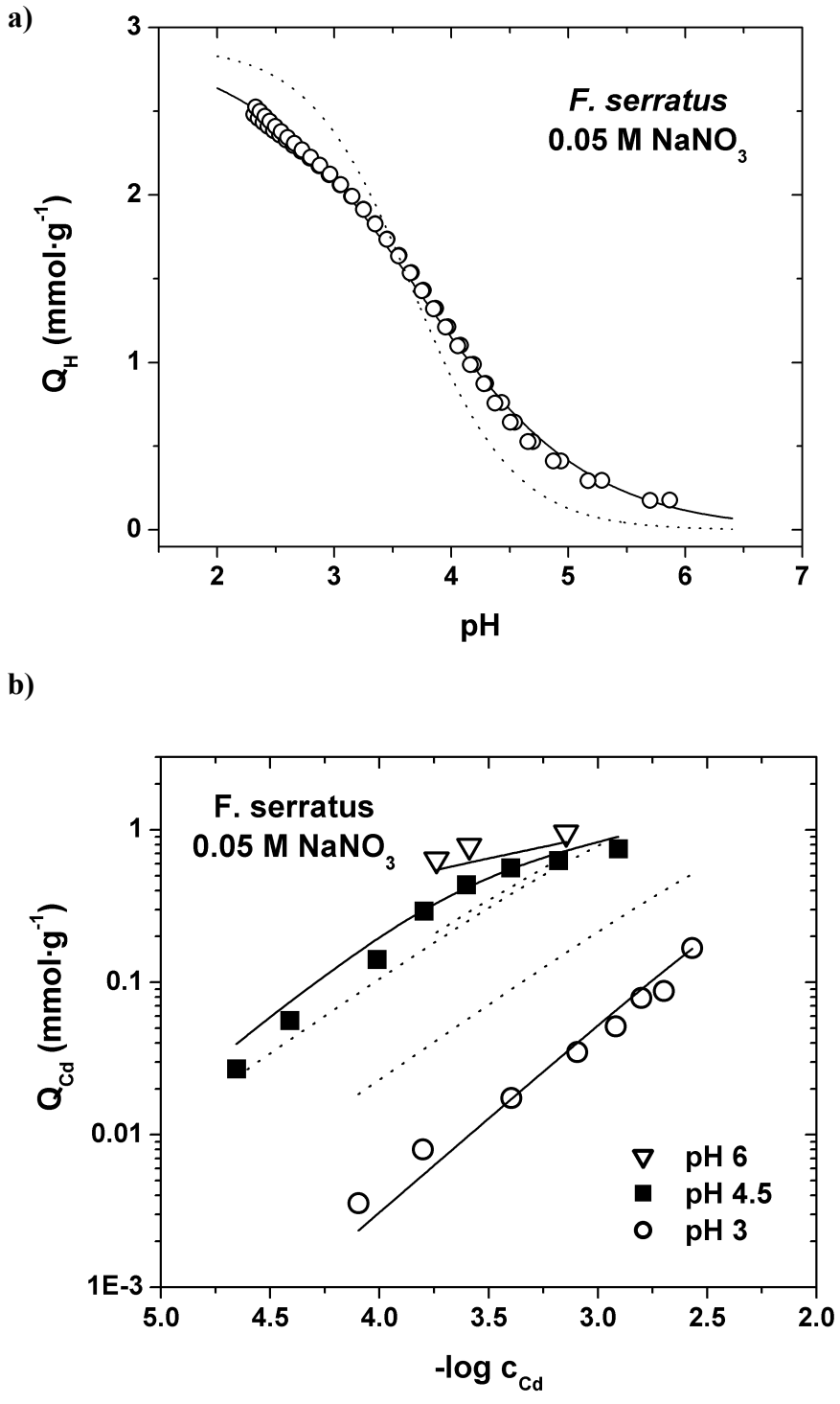

a)
F. serratus
0.05 M NaNO3
Q_H (mmol·g^-1)
pH
b)
F. serratus
0.05 M NaNO3
Q_Cd (mmol·g^-1)
pH 6
pH 4.5
pH 3
-log c_Cd

Figure 2

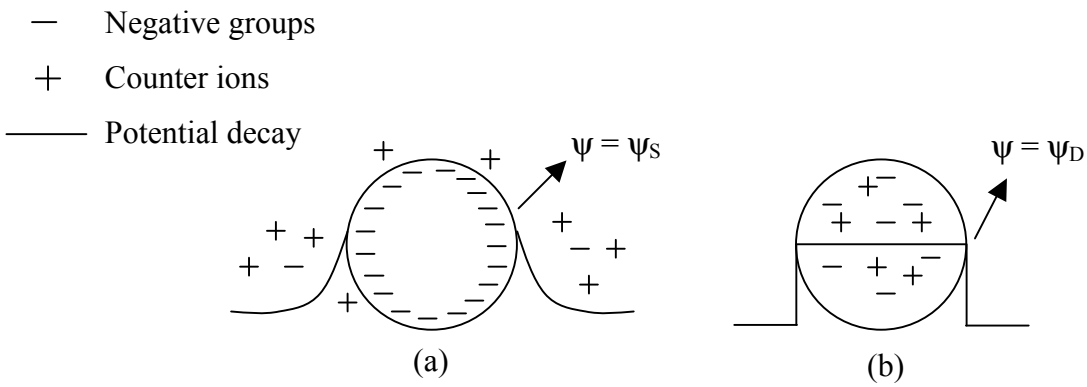


Figure 3

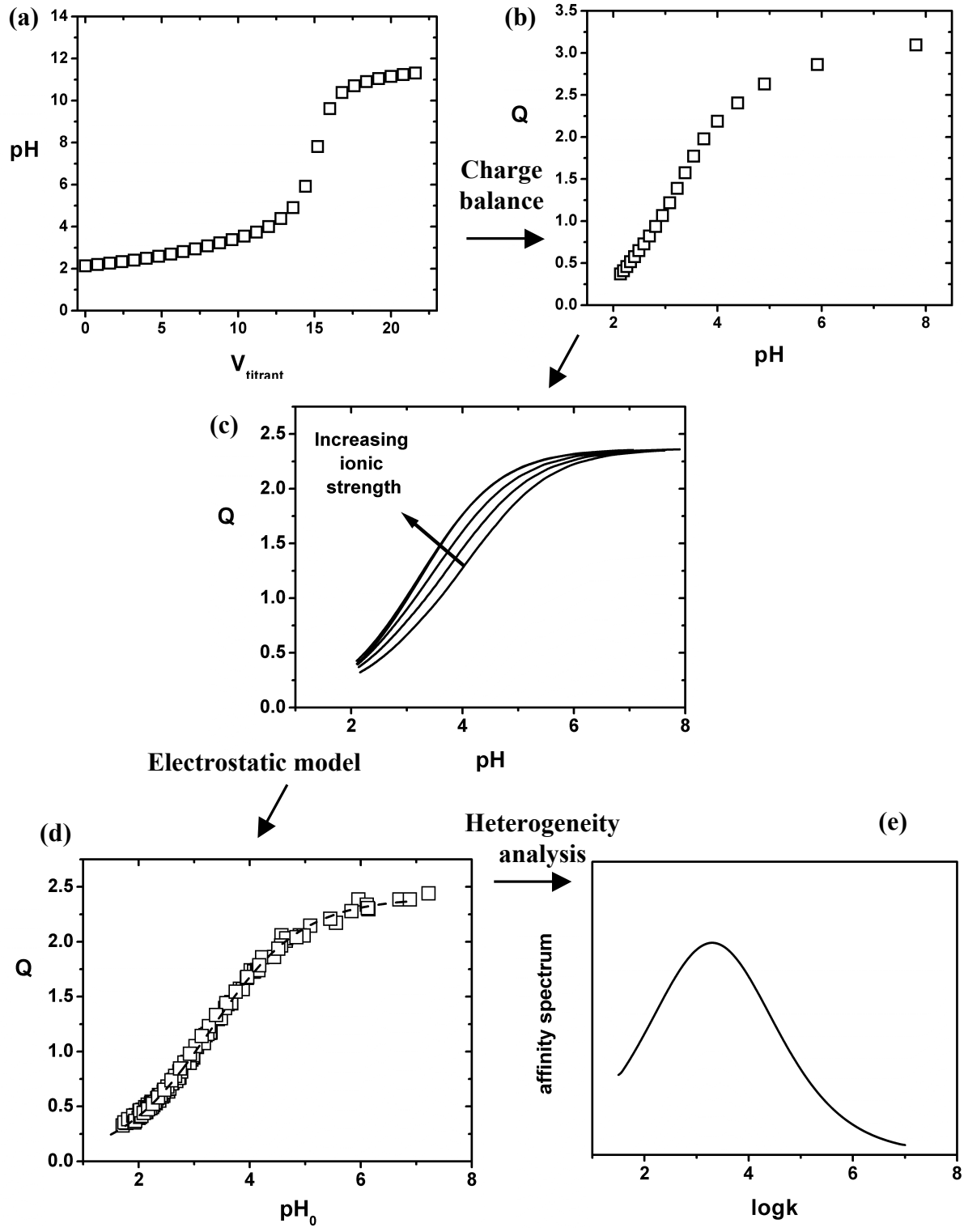
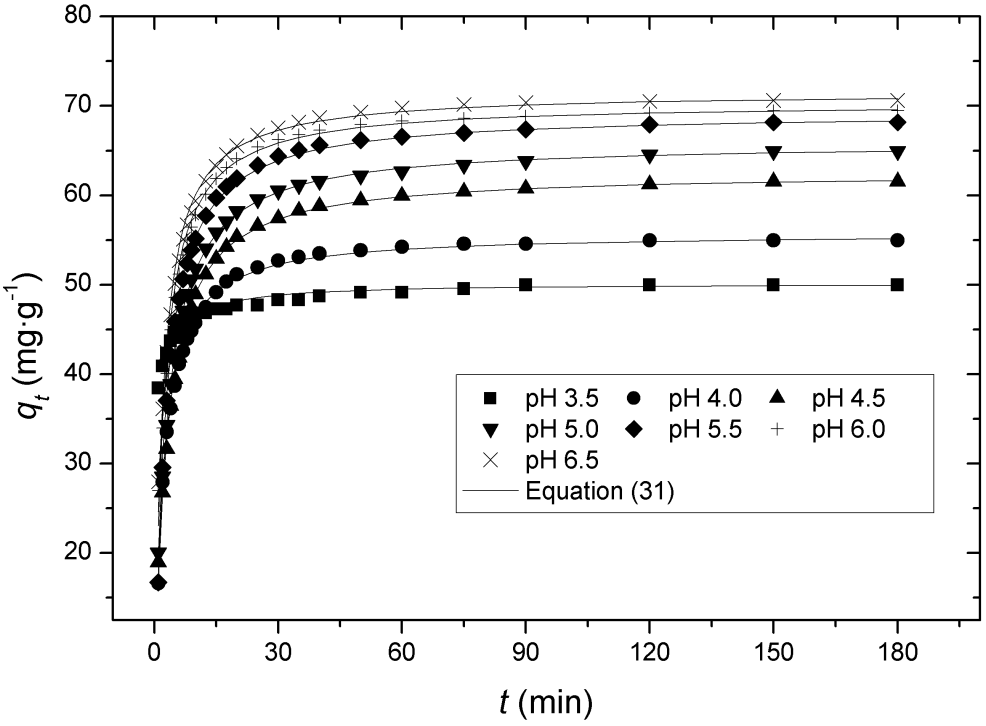

(a)
pH
$V_{titrant}$
(b)
Q
Charge balance
pH
(c)
Increasing ionic strength
Q
pH
Electrostatic model
(d)
Q
pH_0
Heterogeneity analysis
(e)
affinity spectrum
logk

Figure 4


80
70
60
50
40
30
20
q_t (mg·g^{-1})
0
30
60
90
120
150
180
t (min)
pH 3.5
pH 4.0
pH 4.5
pH 5.0
pH 5.5
pH 6.0
pH 6.5
Equation (31)