# Equilibrium and kinetic modeling of metal ion biosorption: on the ways of model generalization for the case of multicomponent systems

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**Abstract** The paper is devoted to the problem of multicomponent sorption of metal ions on the algae-based biosorbents. The basic methods of generalization of the single-component adsorption models are reviewed or introduced and commented for both biosorption equilibrium and kinetics. The problem of similarities and difference between the competitive adsorption and the ion-exchange models is discussed and analyzed to state that both these approaches give the same results providing that only equilibrium properties are considered.

## 1 Introduction

Biosorption is a technique based on employing materials of biological origin (e.g., algae, fungi, bacteria) to immobilize pollutants contained in aqueous solutions (Vegli\u00f3 and Beolchini 1997; Volesky 2001; Volesky and Holan 1995). In particular, it can be applied to remove heavy metal ions (copper, lead, mercury, cadmium, nickel,···). Recently there have been published numerous papers dealing with the biosorption phenomena focusing on experimental studies of binding of heavy metal ions (e.g., $Pb^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Hg^{2+}$) by biosorbents based on the algal biomass or containing the alginates (Ahmady-Asbchin and Jafari 2012; Areco et al. 2012; Cirik et al. 2012; Flouty and Estephane 2012; Ibrahim

2011; Singh et al. 2012; Sulaymon et al. 2012; Wang et al. 2012; Yal\u00e7\u0131n et al. 2012; see also the review by Febrianto et al. 2009). When considering the biosorption systems containing several metal ions able to be bound by the biosorbent, only very few of them have been subjected to profound theoretical analysis of the experimental data. In most cases only several simple (sometimes empirical) mathematical expressions are applied in parallel to correlate the measured data. Such situation does not help draw any more conclusions about the biosorption process mechanisms.

Many attempts have been made to formulate general mathematical expressions or theoretical models, which would be able to adequately describe the equilibrium and kinetics of sorption in the metal ion/biosorbent systems. The overview of the potential models which can be applied in the single-component systems can be found in refs. (Plazinski et al. 2009; Febrianto et al. 2009). Here we focus on the issue of transforming the existing adsorption/sorption/biosorption models in order to describe the multicomponent sorption of metal ions by biosorbents. The systems taken into consideration are those containing (heavy) metal ions and biosorbents based on alginates. This includes algal-biosorbents or alginates (e.g., calcium alginate which can be used directly as the sorbent or as the immobilizer for other types of sorbents) which are both referred to as 'biosorbents' here.

The main aims of this paper are:

(1) To present the brief review of the methods of generalizing the single-component-related models of sorption on the case of sorption systems containing more sorbing species and to comment on the existing ways of such generalization.

(2) To prove the equivalency of the competitive adsorption and ion-exchange equilibrium-related models for the multicomponent systems.

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(3) To put the problem of multicomponent (ad)sorption models into the context of binding of metal ions by the algae-based biosorbents (biosorption).

## 2 Specific binding

The process of cation binding by the biosorbent can be expressed by the following reaction:

$$M + a_M S \longrightarrow K_M MS_{a_M} \tag{1}$$

in which the metal ion (M) valence is not shown; S is the monovalent binding site and $K_M$ denotes the metal ion binding affinity constant. If several different types of ions capable of binding to the biosorbent exist in the system, the additional reaction (in analogy to Eq. 1) must be added to complete the description. The most common situation (in the case of algal biosorbents) is when binding of heavy metal cations is accompanied by binding of protons. In other words, the influence of pH is accounted for by considering the reaction of $H^+$ with the titratable sites of the biosorbent. The usual procedure of arriving at the (bio)sorption isotherm equation consists of: (i) formulation of reactions analogous to Eq. (1) for all species which may be sorbed in the considered system; (ii) finding the appropriate balance equations linking e.g., the total amount of sorbates or the total number of binding sites; (iii) solving the obtained system of equation with respect to the quantity (quantities) of interests (usually, the amount adsorbed in the function of sorbate concentration(s)). Such procedure leads to the set of equations analogous to Eq. (2):

$$K_M = \frac{q_M}{C_M \left(N_s - \sum_i a_i q_{M_i}\right)^{a_M}}. \tag{2}$$

in which $q$ is the amount adsorbed, $C$ is the concentration in the bulk phase, while the subscript denotes the corresponding species. $N_s$ is the total number of binding sites onto the (bio)sorbent surface. The summation includes all species which can be bound by the biosorbent.

The above-described procedure is rather straightforward and intuitive, but there are several (additional) complications which must be considered:

(1) The stoichiometry of binding reaction is not obvious even for the relatively simple system containing raw alginate as the biosorbent; in the case of raw algae or other biosorbents the situation is more complicated by the presence of (at least) several different types of binding sites which contribute to the overall metal ion binding. For instance, the experimental data indicate that at least two different binding modes (mono- and bidentate-, with respect to the carboxyl moieties) are

possible during calcium ions binding by alginate (Papageorgiou et al. 2010). The common procedure of accepting the dentacy of metal-biosorbent complex as equal to the binding ion charge is not justified. Further, the binding of ion may occur according to various schemes proceeding in parallel. If the stoichiometries of binding are known, the only complication connected with the generalization for the case of multicomponent binding is the requirement of considering additional reactions.

(2) The relation linking the total number of binding sites with that occupied by different species is the simplest when assuming that exactly the same sites are equally well accessible for all considered species. This may not be true for the ions differing much in their properties (dimension, charge) for many reasons (e.g., steric hindrance or affinities). Thus, the subsets of binding sites characteristic of each type of ions may be partially separable. The example is the competitive sorption of metal ions ($Pb^{2+}$) and protons which may compete for the same type of binding sites (carboxyl groups) but, additionally, (according to some experimental studies (Davis et al. 2008a)) $Pb^{2+}$ may be sorbed by other oxygen atoms (e.g., hydroxyl or ring oxygens).

(3) The related problem is the chemical heterogeneity of binding sites which may have various characters for each of the sorbing ions. One can distinguish the cases of correlated and uncorrelated affinity distribution functions (Plazinski and Rudzinski 2011). Such distinction is convenient for mathematical modeling purposes but is only a crude approximation.

(4) Other species which do not directly compete with the sorbing ions for the available binding sites may also interfere with the sorption equilibrium. Here one can distinguish two independent cases:

(i) The presence of ligands in the bulk solution competitive for metal ions with respect to the biosorbent binding sites. These may be water molecules (hydrolyzing metal ions) or other strong bases present in the solution (e.g., $OH^-$ ions reacting with metal cations producing metal hydroxide at high pH values). It is worth noting that the products of hydrolysis may also be bound by the biosorbent (Plazinski and Rudzinski 2010).

(ii) The increased values of ionic strength which may be caused by the presence of both sorbing and non-sorbing ions (e.g., 'light' metals and anions). This issue is described in detail below, in the Sect. 3).

(5) It is very probable that obtaining a simple and compact mathematical equation expressing the amount adsorbed in the function of concentrations

of all species of interests will not be possible. Thus, the concept of the biosorption process modeling may be equivalent to the numerical solutions of the set of equations at fixed values of operational parameters.

There exist several methods capable of approximating modeling of issues listed above in points 2 and 3 (Plazinski 2012). The non-ideal competitive adsorption model (NICA) approach and its subsequent modification may be useful in most cases (Koopal et al. 2005; Milne et al. 2003; Rey-Castro et al. 2003). Note that, in most cases, simple mathematical expressions for $q$ are possible to obtain only for monodentate binding.

Finally, let us mention the problem of the biosorption mechanism interpretation. In numerous cases researchers try to distinguish between the ion-exchange (IE) and the adsorption mechanisms. Such distinction makes sense only if there are at least two sorbing ions in the system. The proper identification of the mechanism is obviously important from the point of view of sorption process understanding but if the main aim is the proper prediction of the equilibrium properties, this may not be relevant. Recently it has been proved that the relations describing equilibrium in the binary sorption system are basically the same, independently of the accepted mechanism of ions binding (i.e., IE or adsorption). In other words, it is not important HOW the equilibrium is reached once it is reached. The influence of mechanism is significant only when considering: (i) the non-equilibrium properties (sorption kinetics, difference between the initial and final composition of the bulk and adsorbed phases, etc.); (ii) chemical heterogeneity of the biosorbent related to the distribution of the affinity constant(s). Both these issues are described in detail in Refs. (Plazinski 2010; Plazinski and Rudzinski 2011).

In our previous paper (Rudzinski and Plazinski 2010) we demonstrated the convergence of IE and adsorption mechanisms in the binary system, on the basis of competition between metal ions and protons. Here the more general proof for the case of multicomponent (ad)sorption is presented. Let us consider the system containing $n$ ions able to be bound by the same type of binding sites S equally well accessible for each type of ions. Let us limit ourselves to only two (arbitrary chosen) ions X and Y bound purely by the adsorption process (Eq. 1). The amount adsorbed according to such mechanism will be denoted as $q^{(Ad)}$. As both Eqs. (1) and (2) hold, the appropriate relations read:

$$K_X = \frac{q_X^{(Ad)}}{C_X\left(N_s - \sum_i a_i q_{M_i}\right)^{a_X}},$$ (3)

$$K_Y = \frac{q_Y^{(Ad)}}{C_Y\left(N_s - \sum_i a_i q_{M_i}\right)^{a_Y}}.$$ (4)

Obviously, both competing ions can be bound by the direct adsorption onto the free binding site (which is fully physical assumption if they exhibit any affinity for the biosorbent binding sites). On the other hand, the ion-exchange process between ions X and Y leading to the binding of the X ion can be written as:

$$a_Y X + a_X Y S_{a_Y} \xrightarrow{\kappa} a_Y X S_{a_X} + a_X Y$$ (5)
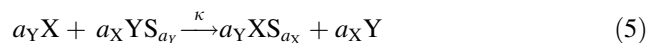
Thus, the relation describing the dependence of the amount adsorbed according to this process ($q^{(IE)}$) can be written as:

$$\kappa = \frac{\left[q_X^{(IE)}\right]^{a_Y} C_Y^{a_X}}{\left[q_Y^{(IE)}\right]^{a_X} C_X^{a_Y}}.$$ (6)

The resulting Eqs. (3)–(5) seem to be quite different but it is the matter of the parameters included in their mathematical forms. Eq. (3) or (4) expresses the amount of the bound ion as the function of its concentration in the bulk phase and the number of free (unoccupied) binding sites. Eq. (6) performs the same operation on the bulk concentrations and amounts adsorbed of two (bound and exchanged) types of ions. After eliminating the common variable (i.e., the number of free binding sites) from Eqs. (3) and (4) and after the simple algebraic transformations one obtains the equation:

$$\frac{(K_X)^{a_Y}}{(K_Y)^{a_X}} = \frac{\left[q_X^{(Ad)}\right]^{a_Y} C_Y^{a_X}}{\left[q_Y^{(Ad)}\right]^{a_X} C_X^{a_Y}}$$ (7)

which is essentially identical to the ion-exchange-related expression (5). The common form of both these equations is the proof that both adsorption and ion-exchange models are mathematically equivalent when applied to the systems in which the equilibrium is reached. The interpretation of the ion-exchange constant $\kappa$ has the form of the l.h.s. of Eq. (7).

The above reasoning is of a general character, as derived from the fundamental mass-action-law on the assumption of general binding stoichiometries. Further, similar transformations can be made for any pair of ions present in the system making the final conclusion general in the case of not only binary but also multicomponent sorption systems.

## 3 Non specific binding

Apart from the specific binding which can be described by the binding reaction analogous to Eq. (1), one can distinguish

also the non-specific one. The non-specific binding effects are connected with the electrostatic attraction between positively charged ions and the negatively charged biosorbent gels (Rey-Castro et al. 2003; Kalis et al. 2009). Both calcium alginate and the algal biosorbents can be treated as gels formed by the polymer chains bearing negative electric charge with the spaces between them filled with water and ions (Donnan gels). The gel particles are assumed to be large enough to assume that the total charge of alginate chains is fully compensated by both bound and free cations present in the gel volume. The non-specific binding can be qualitatively described as the increase of the cation concentration in the gel phase, not connected with the formation of the cation-biosorbent complexes.

The quantitative description requires incorporating the Donnan theory. The concentration (activity) of any ionic species (Z), bearing the charge $z_Y$, in the gel phase depends on the dimensionless concentration factor ($\Lambda$) according to the following relation (Davis et al. 2008b):

$$\frac{[Z^{(P)}]^{1/z_Y}}{[Z]^{1/z_Y}} = \Lambda = \exp\left(-\frac{F\psi(I)}{RT}\right), \tag{8}$$

where the (P) superscript denotes the activity in the gel phase, $\Psi I$ is the Donnan potential [expressed in (V) and being a function of ionic strength, $I$] and $F$ is the Faraday constant. $R$ and $T$ have their usual meanings. Equation (8) holds for both cationic ($\Lambda > 1$) and anionic ($\Lambda < 1$) species. The concentration of neutral species is not affected by the Donnan effects ($\Lambda = 1$). The $\Lambda$ values are possible to be determined experimentally as was done for the $Cd^{2+}$/calcium alginate gel system by Davis et al. (2008b). The obtained values of $\Lambda$ vary from 2.5 to 4.2 (depending on the value of $I$).

Thus, the biosorbent has a contact with the part of the system (i.e., the solution in the gel phase) characterized by higher metal cation concentrations than those monitored during the direct measurements. The $q = f(C_1, C_2, \cdots)$ dependencies presented in the previous section no longer correspond to the real, thermodynamic equilibrium between ions in the bulk solution and those bound by the biosorbent. The consequence of this is that the equilibrium constants characterizing the metal-biosorbent affinity are just the 'conditional' constants, dependent on $\Psi$. As the real, intraparticle concentration is higher than that in the bulk solution, the estimated ('apparent') affinities will be lower than the actual ('intrinsic') ones. Let us also note that although the non-specific binding may be nearly meaningless for estimating the total amount of bound ions (such scenario occurs for the systems with the small Donnan gel volume/volume of solution ratio) it can seriously affect the values of affinity constants.

The 'shift' of the monitored affinity constant values is only one of the results of the Donnan effects. Furthermore, the amount of non-specifically bound ions has to be taken

into account, especially if the volume of the biosorbent particle (associated with the volume of the Donnan gel) is large in comparison to the overall system volume. In such case the amount of the non-specifically bound ions can contribute significantly to the total number of the ions removed from the solution (actually only the latter parameter can be directly monitored). Another observation is that both cationic and anionic species concentrations are affected by the Donnan effects. This may be especially important if there exist other (anionic) ligands, competing with the biosorbent binding sites for metal ions (the most common case is the biosorption occurring at high pH values and the possible precipitation effects).

When there are several types of ions in the system, their intraparticle concentrations are scaled according to the relation $C \rightarrow C\Lambda^z$. This means that in the case of the simplest model (i.e., the multicomponent Langmuir adsorption) the $q_X/q_Y$ ratio as well as that of the corresponding affinity coefficients remains unaffected for each X/Y pair provided that X and Y species have the same charge. Such situation occurs for the very common case of binding various divalent metal ions by the alginate-based biosorbents. The order of affinities of alginic acid for the divalent metal ions reported by Haug (1961) ($Pb^{2+} > Cu^{2+} > Cd^{2+} > Ba^{2+} > Sr^{2+} > Ca^{2+} > Co^{2+} > Ni^{2+} > Mn^{2+} > Mg^{2+}$) remains correct, independently of considering the apparent (i.e., Donnan effects-affected) or intrinsic affinity constants. In the case of the ions characterized by different charges, the analogous scaling occurs via the relation: $q_X/q_Y \rightarrow q_X/q_Y\Lambda^{z_X-z_Y}$. No relatively simple expression is possible to obtain for the slightly more complicated case of the multicomponent adsorption.

Accounting for the non-specific binding usually requires adding more best-fit parameters to the model (e.g., volume of the gel). In some cases, the values of these parameters can be obtained due to the additional experiments (Schiewer and Volesky 1997, Davis et al. 2008b). Moreover, the detailed mass-balance related to the ions present in the solution causes that the corresponding equations have to be solved iteratively.

## 4 Kinetics

The process of metal ion biosorption kinetics in the multicomponent systems may be modeled by using several different approaches, e.g., the intraparticle diffusion models (Suzuki 1990; Crank 1975) or the statistical rate theory approach (Ward et al. 1982). Here we do not consider the even more popular pseudo-first and the pseudo-second order equations due to the following facts: (i) they are only the empirical expressions able to approximate well the behavior predicted by many different theoretical models

(Plazinski et al. 2009); (ii) their mathematical form considers the presence of only one type of sorbing species. In combination with (i), this results in serious complications when trying to generalize these two expressions for the case of the multicomponent sorption.

The case of the intraparticle diffusion-driven kinetics may be considered as relatively simple, as the diffusion of each type of ions in the biosorbent particle can be safely assumed as independent of the diffusion of the remaining species. This is due to the fact that the considered metal ion concentrations are usually very small. Then the theoretical description of the sorption kinetics of $n$ ions simplifies to solving the set of partial differential equations accompanied by adjusting $n$ diffusivities:

$$D_i \nabla C_i(t) = \rho \frac{\partial q_i(t)}{\partial t} \tag{9}$$

where $D_i$ is the diffusivity of the $i$th species in the biosorbent particle and $\rho$ is the particle density, $q_i$ and $C_i$ are the intraparticle (local) concentrations of bound and free ions, respectively; $i$ can vary from 1 to $n$. These equations are not fully independent of each other; they are connected via the $dq/dt$ expression which can be calculated from the equilibrium sorption isotherm equation (according to the local equilibrium assumption, i.e., $dq/dt = dq/dC \cdot dC/dt$). Consequently, such equation written for the multicomponent system contains the concentrations of all the sorbing species. The postulated independence of the diffusion coefficients of the concentration of the other species may not be justified when one considers the rate of sorption of cationic species exhibiting the unusually high affinity for anionic binding sites. Then, the gel charge density changes as the process proceeds. What is more, the interaction of the alginate chains with the rest of the species and other properties (e.g., particle density) may change as well. However, such situation should be considered as rather improbable, as the experiments are carried out by using small amounts of removed ions and those which are present in larger amounts and/or are able to change the gel properties (e.g., calcium ions, protons) are already in equilibrium with the biosorbent before the beginning of the kinetic experiment. Therefore, their diffusion does not have to be taken into account.

Much simpler is the case when one can use the approximate expressions describing the diffusion driven kinetics of sorption derived on the additional assumptions (e.g., the linear sorption isotherm equation for all sorbates). In such a case the rate equations written for each species are truly independent of each other. The presence of other species is accounted for only by the value of $q_e$, calculated from the equilibrium relationship (or directly measured during the experiment). As there exist numerous mathematical expressions derived on different assumptions (e.g., the constant of time-dependent sorbate concentration, varying particle geometry, etc.) the reader is

referred to (Suzuki 1990; Crank 1975) for the particular examples of such models.

Finally, it is worth noting that in many cases the intraparticle diffusivity of ions is assumed to be equal to that characteristic of the bulk solution.

The straightforward generalization of the statistical rate theory (SRT) for the case of multicomponent adsorption was proposed by Azizian et al. (2008). Moreover, Refs. (Plazinski 2010; Plazinski and Rudzinski 2009) describe the specific case of binary system (i.e., protons/metal ions) aiming at the description of the pH influence on the biosorption kinetics. The SRT approach links the sorption rate with the chemical potential of ions in the bulk solution ($\mu_b$) and those bound by the sorbent ($\mu_s$). Considering the system containing $n$ components, one has to solve the set of $n$ (ordinary) differential equations and adjust $n$ best-fit coefficients ($K_e$s). Each of these equations is directly connected with the expression describing the equilibrium state in the considered system, due to the method of obtaining the chemical potentials of the particular species. The appropriate rate equation reads:

$$\frac{dq_i(t)}{dt} = K_{e,i} \left[ \exp\left( \frac{\mu_b(C_i(t)) - \mu_s(q_i(t))}{RT} \right) - \exp\left( \frac{\mu_s(q_i(t)) - \mu_b(C_i(t))}{RT} \right) \right]. \tag{10}$$

Note that the presence of other sorbates is included implicitly, in the expressions for $\mu_s$. The specific form of these expressions depends on the accepted model of adsorption equilibria. Also in this case the situation can be significantly simplified when assuming that each of the sorbates is diluted (which essentially is identical with accepting the linear Henry sorption isotherm for each species), one can arrive at the set of $n$ differential equations which: (i) can be solved independently; (ii) provide analytical solutions for each $q_i(t)$.

Finally, let us consider the Langmuir-like kinetics (Langmuir 1918). The general situation is similar to that described in the SRT-devoted paragraph. One has to solve the set of following $n$ ordinary differential equations for the $n$-component system (written for the simplest case of one-site-occupance adsorption model):

$$\frac{dq_i(t)}{dt} = K_{a,i} C_i(t) \left( N_s - \sum_j q_j \right) - K_{d,i} q_i(t) \tag{11}$$

in which $K_a$ and $K_d$ are some temperature-dependent constants. Accepting the linear sorption isotherm equation simplifies the situation again making $n$ equations independent of each other and allowing for more compact analytical expressions.

Let us note that in the case of SRT and the Langmuirian kinetics the appearing concentrations of sorbates are not necessarily those directly monitored during the experimental

measurements. When accepting the Donnan model, they are equivalent to the 'enhanced' concentrations, scaled according to the Donnan factor $\Lambda$. In the case of each presented approach, the equilibrium relationship influences the kinetic modeling which is understandable as the exact kinetic expressions should be able to predict the equilibrium state in the limit $q(t \to \infty)$. Accounting for these effects in the case of intraparticle diffusion-related models requires modifying the boundary conditions for Eq. (9) at the edges of the sorbent particle or introducing another equation accounting for the diffusion through the boundary layer, being the driving force for flux of sorbing species into the (bio)sorbent particle. Such modification satisfies the condition given by Eq. (8).

As mentioned in the previous section, the distinguishing between ion-exchange and competitive adsorption models is not relevant when aiming only at the equilibrium data correlation and not at profound physical interpretation of the obtained constants. As the scenario is different in the case of the (bio)sorption rate, the brief discussion is given on that issue. Let us focus on the Langmuir-like and the intraparticle diffusion-driven kinetics (the SRT-related related description was already been discussed elsewhere (Plazinski 2010)). Assuming that Eq. (5) describes the ion-exchange surface reaction, the corresponding rate equation (for ion X) reads:

$$\frac{dq_X(t)}{dt} = \kappa_{a,X} C_X^{a_Y}(t) q_Y^{a_X}(t) - \kappa_{d,X} C_Y^{a_X}(t) q_X^{a_Y}(t). \quad (12)$$

Note that this equation cannot be transformed into the Langmuir-like form represented by Eq. (11). For instance, the desorption rate is dependent on the concentration of the competitive ion. Furthermore, (in analogy to Eq. 11) the description of the X sorption rate is incomplete unless the corresponding expression for the exchanged ion (Y) will be given; this is because the additional, time-dependent variables appeared on the r.h.s. of Eq. (12) as well as the second stoichiometric coefficient. If Y can be sorbed by other mechanisms (e.g., by direct reaction with the free binding site), the rate expression must be modified accordingly. In spite of different mathematical form of Eq. (12) when compared to Eq. (11) they both require the same procedure (and the similar amount information about the system) to be solved, i.e., the set of following $n$ ordinary differential equations for the $n$-component system has to be formulated and solved.

The assumption of the local equilibrium inherent in the intraparticle diffusion-driven kinetic model leads to another type of model modification when assuming the ion-exchange-driven reaction. The mathematical form of Eq. (9) remains essentially the same as well as the necessity of considering $n$ rate equations written for $n$ species. The competitive adsorption influences the kinetic model through the $dq/dt = dq/dC \cdot dC/dt$ relation. The analogous relation for the ion-exchange model (and the case of the Y ion replaced by the X one) becomes more complicated as $q_X$ depends of both $C_X$ and $C_Y$ which both are also time-dependent. Thus, the procedure of arriving at the $q_X(t)$ function requires: (i) expressing the $C_Y$ as the function of $C_X$, $q_X$ and (eventually) $q_Y$ (this is possible as long as all equilibrium relationships are known); (ii) expressing the $dq_X/dt$ derivative as the function of the abovementioned variables (or their derivatives); (iii) solving the obtained equation (having the form of Eq. 9) as a part of the larger set of equations; at least one of the remaining equations must refer to the Y species and include the variables common for the X-related case. Note also that for physical reasons the initial and boundary conditions holding for X and Y (i.e., for the exchanging and the exchanged ions) have to be different. In most of the cases the Y ion is already present inside the biosorbent particle before the process of X sorption begins (the particular concentrations should be accounted for in the initial condition). Thus, the related differential equations, in spite of their similar mathematical form, may represent opposite processes: the adsorption of X (i.e., the flux of X inside of the (bio)sorbent particle) may be accompanied by the desorption of Y (its flux outside of the particle).

## 5 Concluding remarks

The major part of the presented mathematical models and derivations is of a general character and can be applied for other types of sorption/adsorption systems not containing the algae-based biosorbents. This includes the considerations on the ion-exchange and competitive adsorption models as well as the overview of kinetic models.

The system containing the algae-based biosorbents and metal ions is usually treated as the single-component system and the theoretical description of equilibrium in such a system is performed accordingly. The system is treated as binary usually when the pH effects are studied. The situation in the real systems is much more complicated as they usually contain other potential sorbates and metal ions which cannot be directly bound but interfere in the indirect way (e.g., through increasing the value of ionic strength). There exist many theoretical approaches designed to deal with the competition between the metal ions and proton but the issue of competition between the metal ions is studied less extensively. In the paper we have presented the straightforward generalizations of the single-component adsorption models in the case of multicomponent metal ion sorption by the algae-base biosorbents. Furthermore, we have shown how the ion-exchange and competitive adsorption models reflect each other and give the same expressions for the equilibrium adsorbed amounts. The

difference resulting from the interpretations of these two models in the context of the kinetic processes are also discussed.

The proper description of the multicomponent sorption kinetics depends not only on the choice of the correct kinetic model but also on the accepted model of sorption equilibrium. One (obvious) reason for that is that the equilibrium-related expressions are only the limiting (i.e., correct for the infinite time) forms of the time-dependent, kinetic ones. The second reason is connected with a necessity of including a form of equilibrium-related expressions (e.g., their derivatives with respect to the sorbate bulk concentration) in the kinetic models. The exact calculations of the kinetic isotherms of sorption for each sorbing compound (which requires solving the set of ordinary or partial differential equations) may be replaced by approximate calculations when there exists such possibility. The most common cases are: (i) the low concentrations of the competing sorbents in the bulk phase or their low affinity for the sorbent (e.g., the presence of light metal ions like $Na^+$ competing with heavy metal cations); (ii) much faster rate of sorption of selected compounds when compared to the remaining ones (e.g., the rate of surface protonation/deprotonation reaction is much faster when compared to the rate of heavy metal ions sorption; similarly, the diffusivity of protons is much higher than that of heavy metal ions).

Finally, it is worth emphasizing that the high degree of complexity of the studied systems often leads to introducing the additional parameters describing the (bio)sorption processes. As these parameters are rarely known a priori, usually a best-fit procedure is used to determine their values. When the number of these parameters is high and their obtained values cannot be verified, the model may not be fully reliable; various 'flexible' models based on diverse physical assumptions may work equally well within a very broad range of adjusting parameters.

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