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Misleading information on homogeneity and heterogeneity obtained from sorption isotherms

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Abstract In this paper, the applications and the differences among the widely applied sorption isotherms (Langmuir isotherm for adsorption, competitive adsorption, ion exchange, Freundlich isotherm) are shown. The misleading information obtained by the formal applications of the isotherms is demonstrated using a simple mathematical model of homovalent ion exchange on homogeneous surface. This model calculation clearly reveals that when studying surface accumulation processes, the mechanism of the sorption process has to be determined. The correct thermodynamic interpretation of the data of sorption experiments is possible only if the isotherm is adapted to the sorption mechanism. It is emphasized that the regression values of the applied models themselves provide correct information neither on the surface heterogeneity nor the interactions among the sorbed species. The curved shape of an inadequate applied isotherm gives no information about the heterogeneity. In order to study the energy distribution of surface sites, the thermodynamic equations, including isotherms, has to be selected on the basis of sorption mechanism. All variable quantities involved in the given model (concentrations of the competing substances in all phases) have to be measured experimentally and included into the isotherm.

Keywords Accumulation · Adsorption isotherm · Ion exchange isotherm · Homogeneous surface · Heterogeneous surface

Abbreviations

$1/n$	Empirical constant of Freundlich isotherm
a	Excess adsorbed amount per unit mass of the adsorbent
b and K	Parameters characterizing adsorption energy ($K = 1/b$):
c	Concentration of solution
CEC	Ion exchange capacity
k_F	Empirical constant of Freundlich isotherm
m	Mass
p	Partial pressure
S	Surface sites of solid
V	Volume
z	Number of surface sites (maximum adsorption capacity)
ζ	Number of ion exchange sites
Θ	Surface coverage

1 Introduction

Geological formations can uptake different electrolytes on their interfaces. Since the net surface charge is typically negative, the accumulation of cations is characteristic. The study of cation accumulation provides information on the thermodynamic data of the process. It is important if we want to use these data, which are obtained in laboratory experiments, to predict the sorption and migration processes of cations under field conditions. The thermodynamic data can be determined using sorption isotherms. These isotherms

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express the relations between the equilibrium concentration of the solution and the accumulated quantity on the solid. There are many papers in which the sorption isotherms (such as Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, etc.) are constructed formally, without considering the sorption mechanism. However, the sorption isotherms can be applied under different conditions. The neglecting of these conditions and the sorption mechanisms result in very serious consequences, such as faulty thermodynamic data, sorption ability orders, etc. Some illustrative examples are shown here.

Wu et al. (2009) have studied the sorption of caesium ions on montmorillonite. The main sorption process is the ion exchange between the caesium ions and the cations in the interlayer space of montmorillonite. Neglecting this mechanism, the authors evaluate the experimental results by Langmuir isotherm. This is not correct because the Langmuir isotherm is an adsorption isotherm describing the surface accumulation of one adsorbate on homogeneous surface. Thus, it cannot be applied for ion exchange which is a competitive process between at least two ions. As a result, the thermodynamic data have no meaning.

A special way of the application of the Langmuir isotherms has been presented by Yeddou and Bensmaili (2007). They have applied the different linear forms of Langmuir isotherm for the same experimental data, and found different isotherm parameters. On the basis of the regressions, they have chosen the best fitting Langmuir isotherm; however, the linear forms take into account the concentration data in solid and solution by different weighting. Beside the Langmuir isotherm, Yeddou and Bensmaili (2007) and other authors (e.g. Akkaya 2012; Rani and Sasidhar 2012) have applied Freundlich isotherm, too, which is the adsorption isotherm of ideal heterogeneous surface. Obviously, the isotherms for homogeneous and heterogeneous surface cannot be valid simultaneously.

Another frequent problem is that some papers express the concentration not in moles, but in mass or even in radioactivity (Akkaya 2012) and on the basis of these data they compare the maximum sorbed quantities. For example, the order or the maximum sorbed quantities is: ^{208}Tl > ^{212}Pb + ^{212}Bi > ^{228}Ac > ^{226}Ra (Akkaya 2012). The radioactivity is given by the product of the decay constant and the number of the radioactive nuclides (Kónya and Nagy 2012), and the decay constants of the listed isotopes decreases exactly in this order. Thus, the "sorption order" is really the order of decay constants, and does not express the interfacial chemical properties of the given isotopes. The sorption affinity order can be more complicated if we consider that the ^{208}Tl, ^{212}Pb, ^{212}Bi, and ^{228}Ac are the members of the decay series of ^{232}Th, they are genetically connected, but it is not discussed here.

Of course, in a real sorbent/solution system, it is very important to determine the dominant sorption mechanism, even if both the mass and charge balance is taken into account. The evaluation of the experimental results with different isotherms can obviously assist to find the real sorption mechanism. The formal applications, however, lead to faulty thermodynamic data. In this paper, the consequences of the formal treatment of sorption processes will be discussed. In order to illuminate the problems, a simple mathematical model calculation will be shown.

2 Sorption processes on solid/electrolyte solution interfaces

The interfaces can be thermodynamically treated by the well-defined Gibbs model and sorption isotherm (Everett 1972; Yildrim 2006). The surface tension of the solid/electrolyte interfaces, however, cannot be determined, so the Gibbs sorption isotherm cannot be applied. In practice, the sorption processes can be evaluated by other sorption isotherms, which apply the relations between quantities on the solid and the solution concentrations. Some sorption isotherm have thermodynamic considerations, others are semi-empirical and empirical (Kinniburgh et al. 1983; van Riemsdijk et al. 1986). The correct application of the sorption isotherms requires the consideration of the sorption mechanism. The components of an electrolyte solution can be accumulated on a solid phase as a result of different sorption processes. For example, the cations can be accumulated on negatively charged surface by adsorption or ion exchange and can be precipitation if the thermodynamic conditions (pH, redox potential, concentration, etc.) of the solution and/or the interface allow this process.

Let's see these processes for Me_1 cation with z_1+ charge. Adsorption results in the increase of the cation concentration on the interface due to the operation of surface forces and takes place on the free surface sites:

$$S + Me_1^{z_1+} \rightleftharpoons Me_1^{z_1+} - S \tag{1}$$

where S denotes the surface sites of solid.

One of the most widespread isotherms for the evaluation of the process (Eq. 1) is the Langmuir equation, which was originally derived for the adsorption of gas molecules on planar surfaces (Langmuir 1918):

$$a = z\frac{bp}{1+bp} \tag{2}$$

where a is the excess adsorbed amount per unit mass of the adsorbent, z is the number of surface sites (that is the maximum adsorption capacity), p is the partial pressure of the adsorptive gas, b is the parameter characterizing the adsorption energy.

The Langmuir isotherm is frequently applied for the description of the adsorption of a dissolved substance where the partial pressure of the gas is substituted by the concentration of the solution (c):

$$a = z\frac{bc}{1+bc} \tag{3}$$

In case of the adsorption of the dissolved substance (solid/liquid interface) the reciprocal amount of b can be used ($K = 1/b$):

$$\mathrm{a} = z\frac{\frac{1}{\mathrm{K}}\mathrm{C}}{1+\frac{1}{\mathrm{K}}\mathrm{c}} \tag{4}$$

The surface coverage of the adsorbed substances (Θ) can be defined as $\Theta = a/z$.

The application of the Langmuir isotherm assumes that the adsorption sites have the same energy (Fowler 1935). This means that the surface is homogeneous and there is no interaction between the adsorbed species. These assumptions are generally not fulfilled even in solid/gas interfaces. Moreover, in case of solid electrolyte systems, there are at least two adsorbates: the ion and the solvent (e.g. water molecules). The solvent concentration, however, is usually much greater than the dissolved substance, so this can be considered constant and may be included into the thermodynamic data. In addition, the ions formed by the dissociation of the solvent, such as hydrogen and hydroxide ions in aqueous solutions, can compete with the adsorbing ions.

The Langmuir isotherm can be transformed into linear form (Table 1).

When two or more different cations are adsorbed, competitive adsorption takes place. The adsorption of the Me_2 cation with z_2+ charge can be described as:

$$S + Me_2^{z_2+} \rightleftharpoons Me_2^{z_2+} - S \tag{5}$$

In this case, the competitive Langmuir isotherm is sometimes applied. For the adsorption of Me_1 ion:

$$a_1 = z\frac{b_1c_1}{1+b_1c_1+b_2c_2} \tag{6}$$

By introducing that $b = 1/K$:

$$a_1 = z\frac{\frac{1}{K_1}c_1}{1+\frac{1}{K_1}c_1+\frac{1}{K_2}c_2} \tag{7}$$

Table 1 Linear sorption isotherm for adsorption of one and two ions (competitive adsorption) as well as ion exchange

Sorption process	Isotherm equation
Adsorption of one ion	$\frac{c}{a} = \frac{1}{z}(c+K)$
Competitive adsorption of two ions (competitive adsorption)	$\frac{c_1}{a_1} = \frac{1}{z}\left(c_1 + K_1 + \frac{K_1}{K_2}c_2\right)$
Ion exchange	$\frac{c_1}{a_1} = \frac{1}{z}\left(c_1 + \frac{K_1}{K_2}c_2\right)$

In Eqs. 6 and 7, the indexes 1 and 2 denote the different cations. Similar equations can be written for Me_2 ion, too.

It is very important to note that the adsorbed ions do not necessarily occupy all the surface sites, some sites may be free. This means that the surface coverage (Θ) of the two ions can be less than 1, or in other way:

$$\Theta_{Me_1} + \Theta_{Me_2} + \Theta_{\mathrm{free}} = 1 \tag{8}$$

The competitive Langmuir isotherm equation (Eq. 7) can be transformed to a similar form as the linear form of the simple Langmuir isotherms, such as listed in Table 1. In the case of competitive adsorption, this form is not linear because it depends on the concentration of the competing ion (c_2).

Ion exchange is the equivalent change between the ions on the surface and in the solution. E.g. the exchange between Me_1 cation with z_1+ charge (in the solution) and Me_2 cation with z_2+ charge (on the solid surface) can be expressed as:

$$z_2Me_1^{Z_1+} + z_1Me_2^{Z_2+} - S \rightleftharpoons z_1Me_2^{Z_2+} + z_2Me_1^{Z_1+} - S \tag{9}$$

In case of $z_1+ = z_2+$, the ion exchange is homovalent, in other cases heterovalent.

Similarly to the adsorption of ions, the ion exchange (Eq. 9) can be also described by isotherm equations. An important difference between the adsorption and ion exchange, however, is that in case of ion exchange the surface sites are always occupied by the ions, there are no free surface sites, that is:

$$\Theta_{Me_1} + \Theta_{Me_2} = 1 \tag{10}$$

This fact has an important consequence for the sorption isotherm, as will be discussed as follows. In order to differentiate the competitive adsorption and ion exchange process, the number of ion exchange sites, that is the ion exchange capacity, CEC) is denoted by ζ (remember that the maximum adsorption capacity (Eq. 2) is denoted by z). The surface coverage of the ions can be expressed as:

$$\Theta_1 = \frac{a_1}{\zeta} \tag{11}$$

$$\Theta_2 = \frac{a_2}{\zeta} \tag{12}$$

For the simplicity, Eqs. 11 and 12 consider homovalent exchange. Since the ions occupy all the surface sites:

$$\zeta = a_1 + a_2 \tag{13}$$

According to the classical derivation of the Langmuir sorption isotherm (Yildrim 2006; Kónya and Nagy 2009), when the sorption equilibrium is reached:

$$\frac{\Theta_1}{\Theta_2} = \frac{b_1c_1}{b_2c_2} = \frac{K_2c_1}{K_1c_2} \tag{14}$$

By the combination of Eqs. 11–14, we obtain that:

$$\frac{\Theta_1}{\Theta_2} = \frac{a_1}{a_2} = \frac{a_1}{\zeta - a_1} = \frac{K_2 c_1}{K_1 c_2} \tag{15}$$

The reciprocal of Eq. 15 is:

$$\frac{\zeta - a_1}{a_1} = \frac{\zeta}{a_1} - 1 = \frac{K_1 c_2}{K_2 c_1} \tag{16}$$

By equivalent mathematical transformation, we obtain the ion exchange isotherm (Table 1) which, similarly to the competitive adsorption isotherm, cannot be linear since it depends on the concentration of the competing ion (c_2):

$$\frac{c_1}{a_1} = \frac{1}{\zeta}\left(c_1 + \frac{K_1 c_2}{K_2}\right) \tag{17}$$

Similar equation can be derived for the exchanged cation (Me_2).

Consider the difference between the competitive ion adsorption and ion exchange isotherm (Table 1): the K_1 value in the bracket on the right side of the equations.

Besides Langmuir models, all the adsorption, competitive adsorption, and ion exchange are frequently evaluated by the classical Freundlich model and its improved versions (Kinniburgh et al. 1983):

$$lna_1 = lnk_F + \frac{1}{n} lnc_1 \tag{18}$$

where k_F and $1/n$ are empirical constants. This model considers the surface to be ideally heterogeneous surface, where the energy distribution (heat of adsorption) logarithmically changes as a function of surface coverage. Freundlich isotherm can be valid for homogeneous surface as well, if the sorbed species interact. When the sorbed species attract each other and the surface is homogeneous, the value of $1/n$ is higher than 1 ($1/n > 1$). However, when $1/n < 1$, this can be caused both by the rejection of the adsorbed species or the surface heterogeneity (Haissinsky et al. 1964).

As seen well, the Langmuir and Freundlich models apply two opposite assumptions: the surface is homogeneous (Langmuir) or heterogeneous (Freundlich); there are no interactions among the sorbed particles (Langmuir) or interactions can be possible among the sorbed species (Freundlich). For this reason, the two models cannot be valid at the same time, even if the regression of the sorption isotherms plotted for the experimental data is fairly good. The regressions of both Langmuir and Freundlich isotherms can be especially good if the sorption process is studied in a relatively narrow concentration range because heterogeneous surface can be treated as a composition of homogeneous portions (Jaroniec et al. 1975; Kinniburgh et al. 1983; Kosmulski et al. 1985; Rusch et al. 1997).

Beside the adsorption and ion exchange, precipitation of the ions can also occur.

Depending on the conditions in the solution (pH, concentration, redox potential, etc.), some metal ions can be hydrolyzed and precipitated as hydroxides or oxides, that is a new solid phase is produced. This process is independent of the presence or absence of a solid surface; it is directed by the solution thermodynamics. In the literature, this process is frequently treated as a sorption process, and a so-called adsorption edge is considered as a function of pH and apply sorption isotherm for the quantitative evaluation. However, this process is not real adsorption and the parameters determined from sorption isotherms include the effects of pH, concentration, surface coverage, etc. (Sparks 2003).

When, however, a solid phase originally is in contact with the solution and the precipitation forms colloid particles, they can be adsorbed on the solid. This process can be treated as colloid adsorption (Derjaguin and Landau 1941; Verwey and Overbeek 1948).

Another precipitation process is surface precipitation, which takes place only in the presence of solid phase. Surface precipitation can be monomolecular, co-precipitation, and heteronucleation (Kónya and Nagy 2009).

3 Model calculation for homovalent ion exchange

As discussed previously in Introduction, the sorption processes are frequently evaluated formally by different isotherms. In order to show what kind of missing consequences, including thermodynamic data, are obtained in this way, a model calculation is made here. Homovalent ion exchange ($z_1+ = z_2+$) (Eq. 9) is assumed on perfectly homogeneous surface. For the simplicity, we choose the initial characteristics of the system:

- the mass of the sorbent (m) is 1 g,
- the volume of the solution (V) is 1 dm^3
- the number of ion exchange sites (ζ) is 10^{-3} mol/g
- The ratio of parameters characterizing the sorption energy (Eq. 17) is K_1/K_2 0.2, 1, 5, respectively.

The ion exchange process can be described by the ion exchange isotherm (Eq. 17). We assume different c_1 concentrations and calculate the concentration of the competing ion (c_2) from the sorbed quantity (a_1). Since 1 g and 1 dm^3 are used in the model calculation, and the ion exchange is homovalent, the numerical values are equal, that is $c_2 = a_1$. For this reason, a_1 is substituted into Eq. 17 instead of c_2 and we obtain that

$$\frac{c_1}{a_1} = \frac{1}{\zeta}\left(c_1 + \frac{K_1 a_1}{K_2}\right) \tag{19}$$

Because of the $c_2 = a_1$ substitution, Eq. 19 is correct only numerically, but the values of a_1 can be calculated when assuming different c_1 concentrations. This calculation is as follows. By equivalent mathematical transformation of Eq. 19 we obtain:

$$\frac{1}{\zeta}\frac{K_1}{K_2}a_1^2 + \frac{1}{\zeta}c_1 a_1 - c_1 = 0 \tag{20}$$

Equation 20 is a quadratic equation, and a_1 can be expressed as a function of c_1 by using the formula for solving quadratic equations:

$$a_1 = \frac{-\frac{c_1}{\zeta} \pm \sqrt{\frac{c_1^2}{\zeta^2} + \frac{4K_1c_1}{\zeta K_2}}}{\frac{2K_1}{\zeta K_2}} \tag{21}$$

ζ and K_1/K_2 are constants as assumed previously (homogeneous surface!). If we assume different c_1 values, the appropriate a_1 values are calculated using Eq. 21. Finally, the distribution coefficient (c_1/a_1) versus c_1 function is plotted (Fig. 1).

As seen in Fig. 1, the shape of the isotherms is not linear as predicted previously (there is the concentration of the competing ion (c_2) in the isotherm (Table 1). The relative position of the isotherms depends on the K_1/K_2 values. The slope of the isotherms is different in the different concentration ranges of the solution. It is very important to note that the curvature of the isotherm is frequently considered as the indication of surface heterogeneity. Remember that the model calculation assumes perfectly homogeneous surface! This means that the shape of the ion exchange isotherm alone cannot mean that the surface is heterogeneous.

As mentioned in Introduction, the ion exchange is frequently evaluated by the linear Langmuir isotherm describing the adsorption of one ion. The number of exchange sites (independently of the actual denotation, z or ζ) and the K isotherm parameter characteristic of the sorption energy are determined from the slope and the intercept of the isotherm. If the isotherm is not linear, as in our model so, different linear portions are arbitrarily fitted and the slopes and intercepts of these portions are considered. This procedure is illustrated in case of $K_1/K_2 = 5$ (Fig. 2). (This plot was already used in Fig. 1, the calculations of the points (Eq. 21) are discussed there.)

As seen in Fig. 2, the isotherm can be divided into four linear portions. The slopes and intercepts of the linear portions, the number of exchange sites and "K" isotherms parameters, as well as the input parameters of the model are listed in Table 2.

As seen in Fig. 2 and Table 2, the surface of the ion exchanger seems to be heterogeneous with four different exchange sites. The regressions all of the four linear plots are fairly good ($R^2 > 0.97$). The number of exchange sites, however, is less than the input value even in the highest concentration range. In addition, the so-called "K" values have no physical meaning because they depend on a variable quantity, the concentration of the competing ion (c_2). Therefore, thermodynamic data estimated from the linear portions as well as any other conclusions have no real physical or chemical meaning.

As mentioned in Introduction, beside Langmuir model, the experimental data of sorption processes are frequently plotted by Freundlich model (Eq. 18), too. The sorption isotherms for our model is shown in Fig. 3 when $K_1/K_2 = 5$. The points of the plot (a_1 values belonging to different c_1 concentrations, Eq. 21) are calculated as discussed previously.

As seen in Fig. 3, $\ln a_1$ versus $\ln c_1$ function can be well fitted by Freundlich model, too, $R^2 = 0.998$. As discussed previously, the Freundlich model considers heterogeneous surface, our model, however, assumed homogeneous surface. This contradiction may be interpreted by the value of $1/n = 0.456$. Since $1/n < 1$, the electrostatic rejection of the cations can be suggested, however, we assume in our

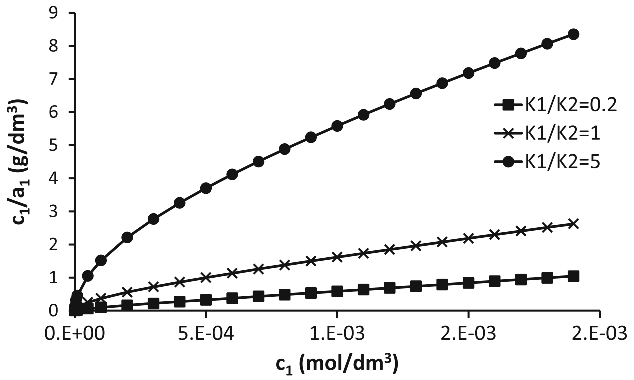

Fig. 1 The distribution coefficient (c_1/a_1) as a function of the concentration of the Me$_1$ ion (c_1) of the homovalent ion exchange (Eq. 17). Input parameters: $m = 1$ g, $V = 1$ dm^3, $\zeta = 10^{-3}$ mol/g, $K_1/K_2 = 0.2$, 1, 5, respectively, $c_2 = a_1$

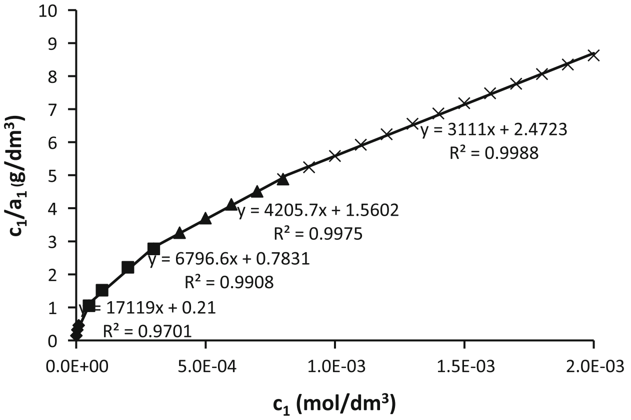

Fig. 2 Linear portions of c_1/a_1 versus c_1 function of the homovalent ion exchange. Input parameters: $m = 1$ g, $V = 1$ dm^3, $\zeta = 10^{-3}$ mol/g, $K_1/K_2 = 5$, $c_2 = a_1$

Table 2 Linear portions of c_1/a_1 versus c_1 function of the homovalent ion exchange

Range of c_1 (mol/dm^3)	Slope (g/mol)	Intercept (g/dm^3)	R^2	ζ (mol/g)	Estimated "K" of the linear portions (mol/dm^3)
1×10^{-6}–5×10^{-5}	17,119	0.21	0.970	5.8×10^{-5}	1.2×10^{-5}
5×10^{-5}–3×10^{-4}	6,796	0.78	0.990	1.5×10^{-4}	1.2×10^{-4}
3×10^{-4}–8×10^{-4}	4,205	1.56	0.997	2.4×10^{-4}	3.7×10^{-4}
8×10^{-4}–2×10^{-3}	3,111	2.47	0.998	3.2×10^{-4}	7.9×10^{-4}
Input parameter				1×10^{-3}	$5 \times c_2$

Input parameters: $m = 1$ g, $V = 1$ dm^3, $\zeta = 10^{-3}$ mol/g, $K_1/K_2 = 5$, $c_2 = a_1$

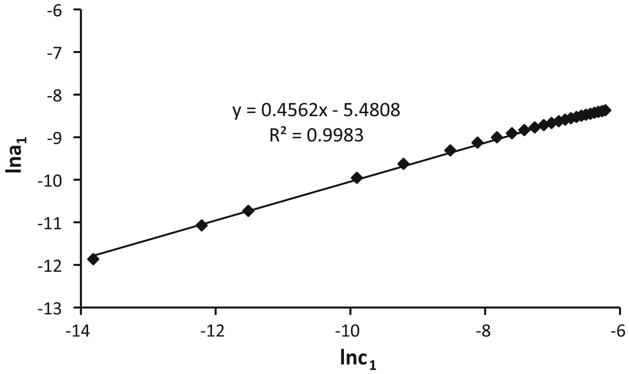

Fig. 3 Freundlich isotherm obtained from the data of homovalent ion exchange (Eq. 18). Input parameters: $m = 1$ g, $V = 1$ dm^3, $\zeta = 10^{-3}$ mol/g, $K_1/K_2 = 10$, $c_2 = a_1$

model that there is no interaction among the sorbed species (this is a basic condition of Langmuir model).

4 Conclusions

During the study of the surface accumulation processes, the mechanism of the sorption process, or at least the dominant process, has to be determined. This is essential during the correct thermodynamic interpretation of the experimental data, including the application of sorption isotherms or any other thermodynamic treatments (e.g. surface complexation models). The regression values of the applied models provide correct information neither on the surface heterogeneity nor the interactions among the sorbed species. Obviously, there are heterogeneous surfaces, but the curved shape of an inadequate isotherm provides no information about the heterogeneity. The simple Langmuir equation cannot be usually applied for competitive sorption processes.

If we neglect the sorption mechanism and apply the thermodynamic treatments formally, the thermodynamic parameters will be not correct; the isotherm equation will give fault values for the number of surface sites and the parameter characteristic for the sorption energy. The homogeneous surfaces can be seen to be heterogeneous just as a result of the application of inadequate sorption models.

In practice, the adequate sorption mechanism is selected considering the chemical and physical properties of the sorbent (e.g. there are exchangeable cations or not); the thermodynamic features of the solution (e.g. pH, concentrations of ions). It is very useful of all variable quantities are measured which are involved in the applied model (e.g. concentration of the competing substances in all phases (Nagy and Kónya 1988) and they are considered as independent variable during the estimation of the sorption parameters.

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