Review

Sorption isotherms: A review on physical bases, modeling and measurement

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Received 6 January 2006; accepted 7 September 2006
Editorial handling by D. Polya
Available online 21 November 2006

Abstract

The retention (or release) of a liquid compound on a solid controls the mobility of many substances in the environment and has been quantified in terms of the “sorption isotherm”. This paper does not review the different sorption mechanisms. It presents the physical bases underlying the definition of a sorption isotherm, different empirical or mechanistic models, and details several experimental methods to acquire a sorption isotherm. For appropriate measurements and interpretations of isotherm data, this review emphasizes 4 main points: (i) the adsorption (or desorption) isotherm does not provide automatically any information about the reactions involved in the sorption phenomenon. So, mechanistic interpretations must be carefully verified. (ii) Among studies, the range of reaction times is extremely wide and this can lead to misinterpretations regarding the irreversibility of the reaction: a pseudo-hysteresis of the release compared with the retention is often observed. The comparison between the mean characteristic time of the reaction and the mean residence time of the mobile phase in the natural system allows knowing if the studied retention/release phenomenon should be considered as an instantaneous reversible, almost irreversible phenomenon, or if reaction kinetics must be taken into account. (iii) When the concentration of the retained substance is low enough, the composition of the bulk solution remains constant and a single-species isotherm is often sufficient, although it remains strongly dependent on the background medium. At higher concentrations, sorption may be driven by the competition between several species that affect the composition of the bulk solution. (iv) The measurement method has a great influence. Particularly, the background ionic medium, the solid/solution ratio and the use of flow-through or closed reactor are of major importance. The chosen method should balance easy-to-use features and representativity of the studied natural conditions.

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0. Introduction

Among all phenomena governing the mobility of substances in aqueous porous media and aquatic environments, the transfer of substances from a mobile phase (liquid or gaseous) to a solid phase is a universal phenomenon. That is the reason why the “isotherm”, a curve describing the retention of a substance on a solid at various concentrations, is a major tool to describe and predict the mobility of this substance in the environment. These retention/release phenomena are sometimes strongly kinetically controlled, so that time-dependence of the sorption isotherm must be specified.

This paper is limited to the retention/release of liquid solutes on natural solid, mineral or organic, materials. The focus is on the interactions of mineral or organic compounds (trace elements, radionuclides, other mineral species such as plant nutrients, and organic compounds such as trace organic non-aqueous or soluble contaminants) with natural mineral or organic materials such as soil, aquifer or geologic material, and suspended particles present in porous media, rivers, lakes and oceans. Many excellent books and papers have reviewed the literature on these mechanisms (e.g. Sposito, 1984; Sposito, 1989; McBride, 1994; Bolan et al., 1999; Pignatello, 2000; Huang et al., 2003), so that this paper deals with chemical mechanisms only when it is necessary for understanding their relation with the isotherm. In contrast, few papers have reviewed some aspects of isotherms themselves (e.g. Schweich and Sardin, 1981; Hinz, 2001), which justifies gathering the theoretical and experimental...
knowledge on sorption isotherms applied to geochemistry.

This review provides some definitions, thermodynamics and kinetics of the reactions involved, then gives an overview on the empirical and mechanistic modeling of both sorption isotherms and kinetics of retention/release, and finally discusses various experimental methods currently available to measure sorption isotherms and reaction kinetics.

1. Definitions

When the retention of a solute on solid particles is investigated, the remaining solute concentration of the compound \( C \) (mol L\(^{-1}\) or kg L\(^{-1}\)) can be compared with the concentration of this compound retained on solid particles \( Q \) (mol kg\(^{-1}\) or kg kg\(^{-1}\)), as shown in Fig. 1. The relationship \( Q = f(C) \) is named the "sorption isotherm". The uniqueness of this relation requires several conditions to be met: (i) the various reaction equilibria of retention/release must have been reached, and (ii) all other physico-chemical parameters are constant. The word "isotherm" was specifically chosen because of the influence of the temperature on sorption reactions; temperature must be kept constant and specified (e.g. Cornelissen et al., 1997; Werth and Reinhard, 1997).

Most of the time, the concentration of the compound retained on the solid is calculated by difference between the initial solute concentration \( C_a_0 \) and the final solute concentration \( C \) (Fig. 1). In the case of retention stage, the solid concentration at equilibrium \( Q \) (mol kg\(^{-1}\)) is given by Eq. (1)

\[
Q = \frac{V}{m} (C_a_0 - C) + Q_a_0
\]

with \( V \) being the volume of solution (L), \( m \) is the solid mass and \( Q_a_0 \) (mol kg\(^{-1}\)) is the concentration of the compound initially retained by the solid, which must be measured or shown to be negligible. In the case of a release stage of a compound that is

![Fig. 1. Schematic view of the adsorption and desorption phenomena. This scheme shows that the final solid concentration \( Q \) can be calculated by difference between the initial liquid concentration (\( C_a_0 \) or \( C_b_0 \)) and the final liquid concentration \( C \) only if the initial solid concentration (\( Q_a_0 \) or \( Q_b_0 \)) is negligible or previously measured.](image-url)
initially present on the solid phase (Fig. 1), the quantity of this initially retained compound \( Q_{b0} \) must be measured previously. The solid concentration at equilibrium can then be calculated by the above equation, replacing \( C_{a0} \) by \( C_{b0} \) and \( Q_{a0} \) by \( Q_{b0} \) (Fig. 1).

In 1888, this approach to represent solute retention on solids was invented by Van Bemmelen (1888). This isotherm often cannot of itself provide information about the type of reaction involved (Sposito, 1984, p. 122; Veith and Sposito, 1977; Scheidegger and Sparks, 1996). For example, the retention can be either due to surface retention without creating three-dimensional structure or to precipitation of a new solid phase (McBride, 1994, p. 141). Sposito proposed to speak about “sorption” to take into account any type or retention (Sposito, 1984, p. 122). The precipitation itself is often induced by surface adsorption (the surface acting as a “template”) and thus called “surface enhanced precipitation” (Wersin et al., 1994; Ford et al., 2002). This phenomenon was shown by James and Healy (1972) and is of major importance in the formation of new solid phases in soils and geologic media (Ford et al., 2002). Due to this diversity of retention mechanisms, it could be more appropriate to use the term “retention isotherm” rather than “adsorption isotherm”. Some authors even propose the term “curve of disappearance of the solute” since the retention is often measured by difference between the initial and final solute concentration (Schweich and Sardin, 1981). It is important to keep in mind that the retention/release mechanisms are various and often intricate (Strawn and Sparks, 1999). From now on, the terms “sorption”, “adsorption”, and “desorption” will be used in their broadest sense (i.e. retention/release) unless otherwise indicated.

2. Reaction kinetics and thermodynamic equilibrium

2.1. Relation between thermodynamics and kinetics

A sorption isotherm is often assumed to be constructed from data obtained at reaction equilibrium. In that case, the adsorption isotherm (made from measurements of progressive adsorption up to the equilibrium) should be the same as the desorption isotherm (made from measurements of progressive release into the solution up to the equilibrium) because the theory of thermodynamic equilibria assumes a complete reversibility of the chemical reactions and so a unique \((C, Q)\) pair (Strawn and Sparks, 1999).

However, sorption mechanisms are driven by several various kinetically controlled reactions or physical phenomena, which have (with redox reactions) the largest variability of reaction times: from few seconds to many years (Sparks, 2000). Fig. 2 shows the energetic variations that occur during adsorption or desorption.

In Fig. 2 is illustrated the standard free energy of the reaction \( \Delta G^0 \) (J mol\(^{-1}\)), which is the difference between the initial state (free solute compound) and the final equilibrated state (adsorbed compound). Thus, \( \Delta G^0 \) is negative since the energy of the system decreases during the reaction to reach a more stable state. The relation between \( \Delta G^0 \) and the reaction constant \( K \) (dimensionless) is given by Eq. (2) (McBride, 1994, p. 14)

\[
K = e^{-\frac{\Delta G^0}{RT}}
\]  

Fig. 2. Energetic state of the solid/solute system during a reaction of adsorption or desorption (adapted from McBride, 1994, p. 27).
with $R$ being the gas constant (J mol$^{-1}$ K$^{-1}$) and $T$ the temperature (K).

In Fig. 2, it is also shown that the thermodynamic equilibrium is the result of a competition between two contrary mechanisms, represented by the activation energy of adsorption $E_1$ and desorption $E_{-1}$. The Arrhenius law (Eq. (3)) provides the relation between the kinetic constants $k$ (dimensionless) and the activation energy $E$ (J mol$^{-1}$) (McBride, 1994, p. 26)

$$k = D e^{\frac{E}{RT}}$$

with $D$ being a dimensionless collision probability factor.

Hence, the relation between the reaction energy of the reaction and the activation energies (Eq. (4))

$$\Delta G^0 = E_1 - E_{-1}$$

can be directly linked with the relation between the thermodynamic constant and the two kinetic constants (Eq. (5))

$$K = \frac{k_1}{k_{-1}}$$

By interpreting Fig. 2, it can be concluded that a reaction can be thermodynamically spontaneous ($\Delta G^0$ negative, $K > 1$), whereas it can be (i) fast, either for adsorption or for desorption (low $E_1$.

Fig. 3. Illustration of different sorption mechanisms of metal ions (Me) on clay minerals by (a) adsorption by outer sphere surface complex on exchange sites located on basal planes (hydrated metal) and as inner sphere surface complexes on the edges (dehydrated metal); or (b) inclusion of the metal into crystal structure by coprecipitation; or (c) precipitation of a new solid phase (after Schlegel et al., 1999a, 2001).
and low $E_{-1}$) or (ii) slow for desorption (high $E_{-1}$) or even (iii) slow for adsorption and for desorption (high $E_1$, higher more $E_{-1}$).

2.2. Kinetic hysteresis and pseudo-irreversibility

It is known that several metals and other heavy elements often show a fast kinetic adsorption reaction by outer-sphere ion exchange followed by slow adsorptions with specific interactions (Aston and Duursma, 1973; Amacher et al., 1986; Bangash et al., 1992; Schlegel et al., 1999b; see Fig. 3). In the case of slow kinetics for desorption (e.g. Nyffeler et al., 1984; Amacher et al., 1986; McLaren et al., 1986, 1998; Bruemmer et al., 1988; Bibak et al., 1995) or for adsorption, too (e.g. Kuo and Mikkelson, 1980; Padmanabham, 1983; Schultz et al., 1987; Backes et al., 1995; Lookman et al., 1995; Smith and Comans, 1996; Schlegel et al., 1999a,b), it is sometimes difficult to know if thermodynamic equilibrium is reached (Smith and Comans, 1996; Sparks, 1998). If not, the superimposition between adsorption and desorption isotherms does not match (Fig. 4). This mismatch between adsorption and desorption isotherms is called “pseudo-hysteresis” or “kinetic hysteresis” (Strawn and Sparks, 1999). A more convenient term could be “apparent irreversibility” (Van Bladel and Laudelout, 1967; McBride, 1994, p. 91; Ford et al., 2002). The common term “irreversibility” can lead to the wrong conclusion that a part of the solute cannot be desorbed at all, whereas it could be a matter of time (Van Bladel and Laudelout, 1967; Ogwada and Sparks, 1986a,b,c; Comans, 1987; Young et al., 1987; Verburg and Baveye, 1994). On the other hand, the saturation capacity of the solid during adsorption can be underestimated if equilibrium is not reached (Harter, 1984). The characteristic time of desorption can be several orders of magnitude different from the characteristic time of adsorption (Bangash et al., 1992; Ainsworth et al., 1994; Smith and Comans, 1996). The adsorbed compound can react, in a second stage, with the solid by (i) slow diffusion inside the solid (e.g. Boyd et al., 1947b;}

![Fig. 4. Pseudo-hysteresis of the desorption isotherm compared with the adsorption isotherm when equilibrium is not reached during the adsorption or desorption stage.](image4)

![Fig. 5. Breakthrough curve of Sr in an organic soil (from Limousin, 2006). If considering the mass balance only, one could conclude erroneously to an irreversible adsorption for half of the Sr injected. However, the presence of a thick tail on the Sr breakthrough curve (while not present for the inert tracer) indicates that desorption is very slow but possibly total.](image5)
Bruemmer et al., 1988; Fuller et al., 1993; Coughlin and Stone, 1995; Burgos et al., 1996; Pignatello and Xing, 1996; Axe and Anderson, 1997; Pignatello, 2000), or (ii) inner-sphere surface complexation (see Fig. 3a; e.g. Benjamin and Leckie, 1981; Lehmann and Harter, 1984; Grossl et al., 1994; Schlegel et al., 1999b; Manceau et al., 2000), or (iii) crystallization of new solid phases (see Fig. 3b and c; e.g. Chrisholm-Brause et al., 1990; Waychunas et al., 1993; Charlet and Manceau, 1994; Manceau et al., 1999; Schlegel et al., 2001). The duration of desorption is increased by the time needed to reverse these reactions. This highlights the importance of knowing the history of a pollution and taking into account the “ageing” effect (Strawn and Sparks, 1999). For the description and the prediction of dynamic phenomena (diffusion through clay materials, advective–dispersive transport through soils and aquifers, particle transport in natural water ...), the measurement of the mean residence time of water in the system is required in order to compare it with the mean characteristic time of the reaction. For example, an apparent “irreversible” adsorption of a long-life radionuclide can often be considered effectively irreversible in aquifers because the water velocity is high, whereas the same adsorption reaction should be considered completely reversible for a long-term waste disposal. Such slow desorption phenomena can be detected by a thick tail of the breakthrough curve during a flow-through experiment, which is on the contrary not present for an inert tracer, as shown in Fig. 5 (Limousin, 2006). In such a case, it is important to lower the background noise as far as possible.

3. Classification and modeling of the isotherms

3.1. The four main types of isotherms

Giles et al. (1974) proposed a general modelling of sorption isotherms, in which 4 particular cases are now used as the 4 main shapes of isotherm commonly observed (Fig. 6).

3.1.1. The “C” isotherm

The curve is a line of zero-origin (Fig. 6a). It means that the ratio between the concentration of the compound remaining in solution and adsorbed on the solid is the same at any concentration. This ratio is usually named “distribution coefficient” or “partition coefficient”: \( K_d \) or \( K_p \) (L kg\(^{-1}\)). The “C” isotherm is often used as an easy-to-use approximation (for a narrow range of concentration or very low concentrations such as observed for trace pollutants) rather than an accurate description. But the simplicity of this isotherm must not justify its use without verification, otherwise it could lead to erroneous conclusions. For example, if the solid has a limited quantity of adsorption sites, the isotherm could be nonlinear because of a possible saturation plateau.

3.1.2. The “L” isotherm

The ratio between the concentration of the compound remaining in solution and adsorbed on the solid decreases when the solute concentration increases, providing a concave curve (Fig. 6b). It suggests a progressive saturation of the solid. One usually makes two sub-groups: (i) the curve reaches

![Fig. 6. The four main types of isotherms (after Giles et al., 1974).](image-url)
a strict asymptotic plateau (the solid has a limited sorption capacity), and (ii) the curve does not reach any plateau (the solid does not show clearly a limited sorption capacity). But it often appears practically difficult to know if an isotherm belongs to the first or to the second sub-group.

3.1.3. The “\(H\)” isotherm

This is only a particular case of the “\(L\)” isotherm, where the initial slope is very high (Fig. 6c). This case was distinguished from the others because the compound exhibits sometimes such a high affinity for the solid that the initial slope cannot be distinguished from infinity, even if it does not make sense from a thermodynamic point of view (Toth, 1995).

3.1.4. The “\(S\)” isotherm

The curve is sigmoidal and thus has got a point of inflection (Fig. 6d). This type of isotherm is always the result of at least two opposite mechanisms. Non-polar organic compounds are a typical case: they have a low affinity with clays. But as soon as a clay surface is covered by these compounds, other organic molecules are adsorbed more easily (e.g. Karimi-Lotfabad et al., 1996; Pignatello, 2000). This phenomenon is called “cooperative adsorption” (Hinz, 2001) and is also observed for surfactants (e.g. Smith et al., 1990; Smith and Galan, 1995; Grosisman et al., 2004). The presence of a soluble ligand can also provide a sigmoidal isotherm for metallic species. At low metal concentrations, the adsorption is limited by the presence of the ligand. The ligand must be saturated and then the adsorption occurs normally (Sposito, 1984, p. 116). The point of inflection illustrates the concentration for which the adsorption overcomes the complexation.

3.2. Modeling of concave isotherms

3.2.1. The Freundlich models

3.2.1.1. Simple Freundlich model. The concave isotherm (“\(L\)” or “\(H\)” isotherms) is the most widely met isotherm. The first model is empirical (Van Bemmelen, 1888; Freundlich, 1909) and is based on the following relation between the adsorbed quantity \(Q\) and the remained solute concentration \(C\) (Eq. (6))

\[
Q = FC^n
\]

with \(F\) (L kg\(^{-1}\)) and \(n\) (dimensionless) being two constants \((n < 1)\). This equation is easily linearizable (Eq. (7))

\[
\log Q = \log F + n \log C
\]

A graph with \(\log C\) as x-axis versus \(\log Q\) as y-axis provides a line of slope \(n\) and intercepts the y-axis at \(\log F\). According to the Freundlich equation, the isotherm does not reach a plateau as \(C\) increases.

3.2.1.2. Modified Freundlich model for competitive adsorption. It is well known that adsorption is subjected to competition between several species (e.g. Murali and Aylmore, 1983c; Roy et al., 1986; Bangash et al., 1992). In order to take into account competitive phenomena, numerous modified Freundlich models have been built, often empirical without any physical basis. For example, several modified Freundlich isotherms (Fritz and Schundler, 1981; Sheindorf et al., 1981) generalize the Freundlich equation to \(m\) competitive species (Eq. (8))

\[
Q_i = F_i C_i \left( \sum_{j=1}^{m} a_{i,j} C_j \right)^{-\frac{n_i}{C_0}}
\]

where \(a_{i,j}\) is the dimensionless competition coefficient of species \(i\) in the presence of species \(j\), and \(F_i\) and \(n_i\) are the coefficients of the Freundlich isotherm of the species \(i\). This formula has been successfully applied to the adsorption of cations (Gutierrez and Fuentes, 1991) and anions in soils (Roy et al., 1986) and to the adsorption of organic compounds on activated organic carbon (Sheindorf et al., 1982).

3.2.2. The Langmuir models

3.2.2.1. Simple Langmuir model. Another very common model is based on reaction hypotheses (Langmuir, 1918). The solid is assumed to have a limited adsorption capacity \(Q_{\text{max}}\). All the adsorption sites (i) are assumed to be identical, (ii) each site retains one molecule of the given compound and (iii) all sites are energetically and sterically independent of the adsorbed quantity. Then, the following reaction is considered:

\[
\text{free site} + \text{solute} \leftrightarrow \text{surface complex}
\]

Since activities of adsorbed species are not clearly defined thermodynamically, the mass action law cannot be directly applied to this reaction. Nevertheless, it has been proposed to assume the surface activity coefficients equal to unity and to calculate the activities with conditional stability constant, where \(Q\) is the solid concentration of
the retained compound on the solid and \( Q_{\text{max}} - Q \) is the solid concentration of the free adsorptive site (Eq. (9))

\[
L = \frac{[\text{surface complex}]}{[\text{solute}][\text{free site}]} = \frac{Q}{C(Q_{\text{max}} - Q)} \tag{9}
\]

Therefore, the “Langmuir” isotherm is (Eq. (10))

\[
Q = Q_{\text{max}} \frac{LC}{1 + LC} \tag{10}
\]

It can be linearized by (Eq. (11))

\[
\frac{Q}{C} = Q_{\text{max}}L - LQ \tag{11}
\]

A graph with \( Q \) as x-axis and \( Q/C \) as y-axis provides a line of slope \(-L\) and intercepts the y-axis at \( Q_{\text{max}}L \). According to the initial assumptions, the isotherm reaches a plateau \( Q_{\text{max}} \) (contrary to the Freundlich isotherm). The constant \( Q_{\text{max}}L \) is the initial slope of the isotherm and \( Q_{\text{max}}L \) is often used as a distribution coefficient \( (K_d) \) when the concentrations are low enough to justify this approximation. The constant \( L \) corresponds to the affinity of the compound for the solid, while \( Q_{\text{max}} \) corresponds to the adsorption capacity of the solid.

3.2.2.2. Modified Langmuir models for multisite or competitive adsorption. Although the Langmuir isotherm is widely used (Travis and Etnier, 1981), its linearization sometimes gives poor results: the graph \( Q/C \) versus \( Q \) often shows a convex curve. Several explanations have been suggested. The first one is the existence of several types of adsorption sites. In that case, it is possible to generalize the Langmuir model to \( p \) couples \((L_i, Q_{\text{max},i})\), each of them corresponding to one type of site (Eq. (12))

\[
Q = \sum_{i=1}^{p} Q_{\text{max},i} \frac{L_iC}{1 + L_iC} \tag{12}
\]

This equation can be linearized part by part by using Eq. (11), providing each couple \((L_i, Q_{\text{max},i})\). The adsorption of phosphate on soils was almost perfectly described by Eq. (12) with two couples \((L_1, Q_{\text{max},1})\) and \((L_2, Q_{\text{max},2})\) (Holford et al., 1974). But several authors have demonstrated that the reciprocity is not true: a perfect adjustment to this model cannot demonstrate a priori the existence of several types of sites (Posner and Bowden, 1980; Sposito, 1982) even if other experiments showed that phosphate is effectively adsorbed by two types of sites. The second explanation to the poor linearity of the function \( Q/C = f(Q) \) is the decrease of adsorption energy as the fraction of occupied sites increases. In that case, the independence between two sites is not valid. The third explanation proposed is the competition between two species. Some continuous open-flow techniques allow flushing the competitive species as soon as they are displaced, limiting their influence (see Section 4.1.2). But it is possible to model an exchange between the added species \( i \) and the displaced species \( j \) (which remains in competition for adsorption). Following this hypothesis, the modification of the Langmuir isotherm yields Eq. (13) (Boyd et al., 1947a)

\[
Q_i = Q_{\text{max},i} \frac{L_iC_i}{1 + L_iC_i + L_jC_j} \tag{13}
\]

This equation was then generalized (Murali and Aylmore, 1983a,b,c) for the competition between \( q \) species (Eq. (14))

\[
Q_i = Q_{\text{max},i} \frac{L_iC_i}{1 + \sum_{j=1}^{q} L_jC_j} \tag{14}
\]

According to this formula, the saturation capacity \( Q_{\text{max}} \) is not affected by competition (the different species being adsorbed by the same adsorptive sites) and a simple Langmuir isotherm can be used to obtain it. On the contrary, the affinity constant \( L_i \) is influenced by the competitive species (Harter and Baker, 1977). Murali and Aylmore (1983a) used different particular cases to simplify this equation. However, when the competitive phenomenon is ion exchange, the ion exchange isotherm approach should be preferred (see Section 3.5).

3.3. Generalized modeling of any isotherm

In most cases where the concentration of the studied compound is higher than a trace concentration, neither the Langmuir nor the Freundlich isotherms are consistent with the data and more complicated models must be applied (Kinnibuirgh, 1986). Hinz (2001) proposed an equation that could describe any type of isotherm (Eq. (15))

\[
Q = Q_{\text{max}} \sum_{i=1}^{\omega} f_i \prod_{j=1}^{r_i} \left( \frac{A_{ij}C_{\omega,j}}{1 + B_{ij}C_{\omega,j}} \right)^{r_{ij}} \tag{15}
\]

where \( Q_{\text{max}} \) denotes the asymptotic amount of adsorption at high concentrations, \( f_i \) is the fraction of sites of type \( i \) (whereas the total number of different types of site is \( \omega \)), and \( r_i \) gives the number of interaction terms between the different types of sites. \( A_{ij} \) and \( B_{ij} \) are empirical affinity constants and \( p_{i,j}, q_{i,j} \) and \( r_{i,j} \) are dimensionless empirical parameters.
Although this equation is fully empirical and includes many fitting parameters, it has the advantage of decomposing any isotherm into different types of sites.

On the basis of the Langmuir model, another generalized model for any isotherm was constructed (Sips, 1948, 1950; Sposito, 1984, p. 120; Nederlof et al., 1990). The basic idea is to consider any isotherm as an integral of Langmuir isotherms (Fig. 7a). This integral has a density function \( g(L) \) which corresponds to the statistical distribution of the affinity constant \( L \) (Eq. (16))

\[
Q = \int_{-\infty}^{+\infty} g(L) \frac{LC}{1 + LC} dL
\]

with \( g \) being a miscellaneous density function.

Conceptually, each adsorption site provides an elementary isotherm having its own affinity \( L \) and capacity \( g(L) \). The complete isotherm is seen as the sum of all the elementary isotherms, as shown in Fig. 7a. The function \( g \) has been named a “weighting function” (Sposito, 1980), a “site affinity distribution function” (Kinniburgh et al., 1983), or a “frequency distribution of the local affinity coefficient L’” (Perdue and Lytle, 1983).

By choosing the accurate density function \( g \), any type of isotherm can be described by Eq. (16) (Sposito, 1984, p. 120; Hinz et al., 1994). In the case of the simple Langmuir isotherm, one can isolate \( Q_{\text{max}} \) (Eq. (17))

\[
Q_{\text{max}} = \int_{-\infty}^{+\infty} g(L) dL
\]

According to Eq. (16), \( g \) requires to be a Dirac’s function (Eq. (18)) in order for \( Q_{\text{max}} \) to be a constant

\[
g(\ln(L)) = Q_{\text{max}} \delta(L - L_m)
\]

with \( \delta \) being the Dirac’s function and \( L_m \) the most probable \( L \).

The Langmuir isotherm is consequently the sum of isotherms having the same constant \( L_m \). If the Freundlich isotherm is needed, \( g \) must be a function whose curve closely resembles a log-normal distribution (not detailed here). Hence, one can conceptualize the Freundlich isotherm as the sum of individual Langmuir isotherms (Fig. 7b) with a log-normal distribution of their affinity constants (Sposito, 1984, p. 121; Kinniburgh et al., 1983; Hinz et al., 1994). The same result would be obtained by assuming that the Freundlich isotherm is a derived Langmuir isotherm where the adsorption energy decreases logarithmically as the fraction of occupied sites \( Q/Q_{\text{max}} \) increases (Hasley and Taylor, 1947).

3.4. Isotherms of uncharged organic compounds

Excellent reviews about the adsorption and desorption mechanisms of organic compounds have been written (Pignatello, 2000; Huang et al., 2003). Like many other adsorbed substances, the linear approximation of the isotherm is often suitable at low concentration (e.g. Schwartzenbach and Westall, 1981; Groisman et al., 2004), so that a constant distribution coefficient can be applied. Moreover, non-polar or at least uncharged organic compounds are hydrophobic and mainly adsorb via Van der Waals attractions onto the hydrophobic part of solid organic matter. So, their affinity for the solid is often explained by their affinity for solid organic matter only (e.g. Karickhoff et al., 1979; Schwartzenbach...
When the concentration of the studied ion is low driven by competing ion exchange phenomena. Thus, their adsorption is mainly attracted by the surface charges of the solid. Consequently, the adsorption capacity depends on the cation exchange capacity (resp. anion exchange capacity). When the concentration of the studied ion is low compared to the concentration of other competing ions, the composition of the bulk solution can be considered constant and a single-species isotherm can be applied, although remaining strongly dependent on the composition of the bulk solution. However, when the concentration of the studied ion reaches the same order of magnitude as other competing ions, the composition of the bulk solution can no longer be considered constant and a multi-species isotherm is needed.

It is possible to take into account the competition between several ions with modified multi-species isotherms (see Sections 3.2.1.2 and 3.2.2.2). Murali and Aylmore (1983b) simulated the consequences of different competition features on the shape of multi-species equilibrium or kinetic Freundlich and Langmuir isotherms. The ion exchange isotherm is another way to describe the competition between two or more ions when their range of concentration is wide. This specific isotherm does not describe \( Q \) versus \( C \), but the molar fraction of charges \( E_k \) of the ion \( k \) adsorbed on the solid \((\text{mol c kg}^{-1})/(\text{mol c L}^{-1})\) versus the molar fraction of charges \( E_k \) of the ion \( k \) remaining in solution \((\text{mol c L}^{-1})/(\text{mol c L}^{-1})\). The molar fraction of charges \( E_k \) of an ion \( k \) is defined by Eq. (21)

\[
E_k = \frac{N_k}{N_{\text{total}}}
\]

with \( N_k \) being the normality of ion \( k \) \((\text{mol c L}^{-1})\) and \( N_{\text{total}} \) is the total normality \((\text{mol c L}^{-1})\). The normality of the ion \( k \) is defined as its aqueous concentration of charges (Eq. (22))

\[
N_k = v_k C_k
\]

with \( v_k \) being the valence of ion \( k \) (dimensionless), and the total normality being the sum of normalities of all present ions or, said differently, the total concentration of charges in solution (Eq. (23))

\[
N_{\text{total}} = \sum_k N_k
\]

So, \( E_k \) and \( \bar{E}_k \) vary between 0 and 1, according to Eq. (21).

It is also assumed that the number of adsorption sites (surface charges of the solid) is constant, and is called the “intrinsic charge” of the solid \( \sigma_{\text{int}} \) \((\text{mol c kg}^{-1})\). For a cation (resp. anion) exchange, the adsorption capacity depends on the cation exchange capacity (resp. anion exchange capacity). But it is important to keep in mind that the cation or anion exchange capacity is an operational

3.5. The ion exchange isotherms

The mineral species (which are almost all charged in aqueous solution) are mainly attracted by the surface charges of the solid. Thus, their adsorption is driven by competing ion exchange phenomena. When the concentration of the studied ion is low
parameter and not an intrinsic property of the solid. So, it cannot be defined as $\sigma_{\text{int}}$, which is a conceptual parameter. The anion or cation exchange capacity is strongly dependent on the measurement conditions such as pH or ionic strength (Charlet and Schlegel, 1999; Limousin and Tessier, 2003). To give a realistic value to $r_{\text{int}}$, the best method is probably to measure the anion or cation exchange capacity with one of the studied ions itself.

The ion exchange isotherm is constructed from an exchange between two ions $i$ and $j$, with $N_{\text{total}}$ remaining constant, otherwise the uniqueness of the isotherm is not valid (e.g. Singhal et al., 1976; Schweich and Sardin, 1981). Fig. 8 shows NH$_4$/Ca exchange isotherms on two minerals. In this example, the affinity of hydroxy-Al interlayered vermiculite is stronger for NH$_4$ because the curve is located above the non-preference curve (which represents the equal affinity of the solid for NH$_4$ and Ca), whereas vermiculite does not exhibit significant preference for NH$_4$ or Ca. For a homoionic exchange (two ions with same valence), the non-preference curve is simply the 1:1 line. However, the non-preference curve of an exchange between two ions with different valences is not a line because the purely electrostatic attraction of an ion (without any specific affinity) is proportional to the exponential of its valence, so that the ion of highest valence is more adsorbed. Here the exchange between two ions $i$ (with valence $z_i$) and $j$ (with valence $z_j$) is described

$$z_i \text{solid-}i + z_j \text{free } j \leftrightarrow z_i \text{solid-}j + z_j \text{free } i$$

By similarity with the law of mass action, the selectivity coefficient $K_{\text{ex}}$ is (Eq. (24))

$$K_{\text{ex}} = \frac{[\text{solid-}j]^{z_j}[\text{free } j]^{z_j}}{[\text{solid-}i]^{z_i}[\text{free } i]^{z_i}} \frac{E_{i}^{z_i} E_{j}^{z_j}}{E_{i}^{z_j} E_{j}^{z_i}}$$

(24)

Thus, a non-preference of the solid means that $K_{\text{ex}} = 1$, which leads to the same fixed/free ratio ($E_i/E_j$) for both ions only if $z_i = z_j$. However, Eq. (24) is a way to find a mathematical similarity with the law of mass action, but it cannot be considered as a thermodynamic formula: most of the time, ion exchange deviates from the ideal exchange behaviour, so that the selectivity coefficient $K_{\text{ex}}$ varies significantly with $N_k$ (e.g. Singhal et al., 1976). Thus, $K_{\text{ex}}$ values should always be provided with the range of $N_k$ and ionic strength used for the measurement. Among many formulas modelling ion exchange, a simple analytical model was proposed to describe both ion exchange with possible non-ideal behavior and inner-sphere complexation (Fletcher and Sposito, 1989).

Sometimes the ion exchange isotherm has a point of inflection. It means that the preferential affinity of the solid for one of the two ions shifts to the other ion when the fraction of charges occupied by the first ion reaches a certain value. It can be caused by the existence of two types of sites. A well known example is the K (or NH$_4$)/Ca exchange on the 2:1

---

**Fig. 8.** Ion exchange isotherm: exchange between two heterovalent ions NH$_4^+$ and Ca$^{2+}$ on vermiculite and hydroxy-aluminum interlayered vermiculite, compared with the non-preference curve of a monovalent/divalent ion exchange. The total normality was maintained constant at 1 mol L$^{-1}$ (from Evangelou and Lumbranraja, 2002).

**Fig. 9.** K/Ca exchange isotherm on an Australian soil containing 2:1 clay minerals. The total normality was maintained constant at 0.2 mol L$^{-1}$ (from Bloom and Mansell, 2001).
clays (Fig. 9). For a high fraction of Ca, the ditrigonal sites that are available to ion exchange have a specific affinity for K, and so specifically adsorb this monovalent cation. Then, for a high fraction of K (when all the available ditrigonal sites are occupied by K), the other sites do not have specific affinity and the isotherm tends to reach the non-preference curve of a divalent/monovalent ion exchange (e.g. Beckett, 1964; Jardine and Sparks, 1984; Bloom and Mansell, 2001).

3.6. Surface complexation models

Although this paper is not aimed at reviewing sorption mechanisms, mechanistic models have been markedly improved during the last 20 years and are often used to construct sorption isotherms and to gain mechanistic interpretation of them, including the influence of ionic background (e.g. Sahai and Sverjensky, 1997; Criscenti and Sverjensky, 2002; Sverjensky, 2005). These surface complexation models are based on inner- or outer-sphere complexes, and can be distinguished from each other by the way they represent the distribution of the electric potential around the charged surfaces. The main historical models are: the triple-layer model (Davis et al., 1978), the constant capacitance model (Stumm et al., 1980), the Stern variable surface charge model (Bowden et al., 1980), the one-pK model (Van Riemsdijk et al., 1986), the generalized two-layer model (Dzombak and Morel, 1990), and the charge distribution model (Hiemstra and Van Riemsdijk, 1996). Good reviews have been written on the physical bases and experimental applications of surface complexation models (e.g. Goldberg, 1992, 2004). Thanks to the increasing power of computers, it has become possible to apply these models to many codes such as these free-download programs: MinteqA2 (Allison et al., 1991), PhreeqC (Parkhurst and Appelo, 1999) or Chess (Van der Lee and De Windt, 1999), which are continuously improved and appear now to be essential tools for geochemistry.

3.7. How to choose among so many models?

Table 1 shows the diversity of the formulas that exist to model sorption isotherms at equilibrium and Table 2 provides other formulas modelling the kinetic dependence of adsorption/desorption. These formulas can be included in solute transfer equations such as through-diffusion or advection-dispersion equations (Selim, 1992). The choice of the adsorption/desorption model can have a great influ-

<table>
<thead>
<tr>
<th>Curve shape</th>
<th>Model</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>“C” curve</td>
<td>Linear</td>
<td>( Q = K_d C )</td>
</tr>
<tr>
<td></td>
<td>Linear for the species ( i ), in competition with other species</td>
<td>( Q = \frac{K_d C}{\sum_{j} n_j C_j} )</td>
</tr>
<tr>
<td>“L” or “H” curve</td>
<td>Freundlich</td>
<td>( Q = FC^n )</td>
</tr>
<tr>
<td></td>
<td>Freundlich with competition between two species ( i ) and ( j )</td>
<td>( \bar{Q} = F_i C_i \left( a_i C_i \right)^{n^*-1} )</td>
</tr>
<tr>
<td></td>
<td>Freundlich with competition between ( m ) species</td>
<td>( \bar{Q} = F C \left( \sum_{i} a_i C_i \right)^{n^*-1} )</td>
</tr>
<tr>
<td></td>
<td>Temkin</td>
<td>( Q = K_t \ln(C_t) + K_2 )</td>
</tr>
<tr>
<td></td>
<td>Rothmund–Kornfeld (exchange between two ions ( i ) and ( j ))</td>
<td>( \frac{Q}{\bar{Q}} = K_{ti} \left( \frac{C_t}{C_i} \right)^{\gamma} )</td>
</tr>
<tr>
<td></td>
<td>Langmuir</td>
<td>( Q = Q_{\text{max}} \left( \frac{C_i}{C_{\text{ex}}} \right)^n )</td>
</tr>
<tr>
<td></td>
<td>Langmuir with competition between two species ( i ) and ( j )</td>
<td>( Q = Q_{\text{max}} \left( \frac{C_i}{C_{\text{ex}}} + C_j / C_{\text{ex}} \right)^n )</td>
</tr>
<tr>
<td></td>
<td>Langmuir with competition between ( q ) species</td>
<td>( Q = Q_{\text{max}} \left( \frac{C_i}{C_{\text{ex}}} + \sum_{j} C_j / C_{\text{ex}} \right)^n )</td>
</tr>
<tr>
<td></td>
<td>Langmuir-Freundlich</td>
<td>( Q = \frac{Q}{\bar{Q}} \left( \frac{C_i}{C_{\text{ex}}} \right)^n )</td>
</tr>
<tr>
<td></td>
<td>Generalized Langmuir</td>
<td>( Q = \frac{Q}{\bar{Q}} \left( \frac{C_i}{C_{\text{ex}}} \right)^n )</td>
</tr>
<tr>
<td></td>
<td>Redlich–Peterson</td>
<td>( Q = \frac{Q}{\bar{Q}} \left( \frac{C_i}{C_{\text{ex}}} \right)^n )</td>
</tr>
<tr>
<td></td>
<td>Toth</td>
<td>( Q = \frac{Q}{\bar{Q}} \left( \frac{C_i}{C_{\text{ex}}} \right)^n )</td>
</tr>
<tr>
<td></td>
<td>Hinz</td>
<td>( Q = \frac{Q}{\bar{Q}} \left( \frac{C_i}{C_{\text{ex}}} \right)^n )</td>
</tr>
<tr>
<td>“S” curve</td>
<td>Sigmoidal Langmuir</td>
<td>( Q = \frac{Q}{\bar{Q}} \left( \frac{C_i}{C_{\text{ex}}} \right)^n )</td>
</tr>
</tbody>
</table>

\( C \): aqueous concentration, \( Q \): solid concentration.

From Murali and Aylmore (1983a,b,c), Selim (1999) and Hinz (2001).
Table 2
Some classical kinetic models of adsorption/desorption with analytical formulae

<table>
<thead>
<tr>
<th>Model</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>First order</td>
<td>( \frac{dQ}{dt} = -zk_1C - k_{-1}Q )</td>
</tr>
<tr>
<td>nth order</td>
<td>( \frac{dQ}{dt} = -zk_1C^n - k_{-1}Q )</td>
</tr>
<tr>
<td>Langmuir kinetic</td>
<td>( \frac{dQ}{dt} = \frac{zk_1C(Q_{\text{max}} - Q) - k_{-1}Q}{1 + C/\theta} )</td>
</tr>
<tr>
<td>Langmuir kinetic with competition</td>
<td>( \frac{dQ}{dt} = \frac{zk_1C(Q_{\text{max}} - Q) - k_{-1}Q}{1 + C/\theta} )</td>
</tr>
<tr>
<td>Elovich</td>
<td>( \frac{dQ}{dt} = k \exp(-PQ) )</td>
</tr>
<tr>
<td>Power</td>
<td>( \frac{dQ}{dt} = \frac{kC^nQ^m}{1 + C/\theta} )</td>
</tr>
<tr>
<td>Mass transfer (fraction of immobile water)</td>
<td>( \frac{dQ}{dt} = \frac{k(C - C_{\text{im}})}{1 + C/\theta} )</td>
</tr>
<tr>
<td>First order with partly pseudo-irreversible adsorption</td>
<td>( \frac{dQ}{dt} = \frac{k(C - C_{\text{irr}})}{1 + C/\theta} )</td>
</tr>
</tbody>
</table>

C: aqueous concentration, Q: solid concentration, t: time, \( \theta \): volumetric water content, \( \rho \): bulk density.

From: Murali and Aylmore, 1983a,b,c; Selim, 1999.

ence on the prediction of solute transfer (e.g. Hinz et al., 1994; Brusseau, 1998). An ideal model verifies 4 properties: it must be effective, comprehensive, realistic and predictive (Barrow and Bowden, 1987). Fitting simultaneously all the parameters of a model is obviously the worst solution (Westall and Hohl, 1980; Brusseau, 1998) because many different mechanisms could provide the same breakthrough curve (see Section 4.2.2). A step-by-step method must be applied, trying first to adjust the simplest models (or the most adequate model, based on a mechanistic knowledge of the system) to the data and then choosing a more complex model if needed. If a new parameter is introduced into the model without any physical justification, its accuracy should be verified by testing its sensitivity in different conditions and its physical meaning must be concluded carefully. When it is not possible to fit each parameter separately, it is impossible to give any physical meaning to the parameters, and an adequate criterion must be selected to discriminate each model. Saiers and Hornberger (1996) proposed applying an index named “model selection criterion” (Koeppenkastrop and Decarlo, 1993), or MSC (Eq. (25))

\[
MSC = \ln \left( \frac{\sum_{i=1}^{d} w_i (C_i - C)^2}{\sum_{i=1}^{d} w_i (C_i - C_{mi})^2} \right) - \frac{2\lambda}{d} \tag{25}
\]

where \( d \) is the number of data points, \( \lambda \) is the number of fitted parameters, \( C_i \) is the \( i \)th observed concentration from the replicate experiments, \( C \) is the average of observed concentrations, \( C_{mi} \) is the model-calculated concentration corresponding to the \( i \)th replication, and \( w_i \) is a weighting factor (if needed). The model retained must have provided the highest MSC. This type of quantitative criterion has the advantage of taking into account the number of fitted parameters (which should be as low as possible), as well as a classical least-square calculation.

4. Experimental methods

4.1. Influence of the experimental conditions

A sorption isotherm does not have any intrinsic thermodynamic definition: its significance depends on the conditions from which it is obtained. So, the measurement method has a strong influence on the results and a brief description of it should always be provided with the data (Schweich and Sardin, 1981).

4.1.1. The solid/solution ratio

In many cases, the ratio of solid mass versus solution volume should theoretically not influence the proportion of adsorbed compound. And most of the time, this parameter does not effectively influence the shape of the isotherm if it remains in the same order of magnitude. However, numerous authors observed a significant and nonlinear dependence of the solid/solution ratio on the amount of adsorption (Aston and Duursma, 1973; O’Connor and Connolly, 1980; Di Toro and Horzempa, 1982; Voice et al., 1983; Di Toro, 1985; Tan and Teo, 1987; Boesten and Van der Pas, 1988; Bangash et al., 1992; Bajracharya et al., 1996; Porro et al., 2000). Despite a few contradictory studies (Koss and Kim, 1990), adsorption is often observed to decrease with the solid concentration. This phenomenon is called the “solid effect”. The main reasons proposed are (i) the occupied volume of the suspended particles (Celorie et al., 1989) and (ii) their aggregation (Voice et al., 1983; Di Toro et al., 1986) that would prevent an optimal adsorption of the solutes. For the particular case of clay materials, the cationic exclusion volume increases as compaction increases, so that the solid/solution ratio has an additional influence. The best experimental choice is a solid/solution ratio that is representative of the natural conditions. In the case of water with suspended particles, the solid concentration is often two low to be used in batch. In contrast, the solid/solution ratio of soils and other geologic media is
too high to be used in batch (e.g. the solid/solution ratio of soils is typically 1:1, whereas the solid/solution ratio of aquifers is closer to 3:1 and the packed clay barrier materials have a solid/solution ratio higher than 10:1, up to the limit where only adsorbed water is present), but can be achieved in column experiments. For batch experiments with these natural porous media, the range 1 g of solid for 2 mL to 1 g of solid for 4 mL is advised (Porro et al., 2000). But for strongly adsorbed compounds, this ideal solid/solution ratio is sometimes too high to detect the compound remaining in solution. In conclusion, the choice of an adequate solid/solution ratio consists of finding a good intermediate between experimental constraints and representative conditions.

4.1.2. Closed reactor versus open flow

The isotherms obtained with flow-through experiments are often consistent with batch data (e.g. Bond and Phillips, 1990; MacIntyre et al., 1991). However, the removal (or not) of the solution, i.e. maintaining (or not) a constant composition of the solution, can influence the quantity of adsorbed compounds. In batch or in re-injected flow methods, the displaced competitive substances remain in solution, and thus may interact with the solid. In contrast, the open-flow methods supply the system with a constant solution and the displaced substances are flushed out and thus do not compete for adsorption. Therefore, adsorption should be higher for the open-flow methods such as column or stirred-flow through reactor (Akratanakul et al., 1983). Some authors have observed this phenomenon (Akratanakul et al., 1983; Miller et al., 1989b; Porro et al., 2000; Gabriel et al., 1998: see Fig. 10). But many other studies show that the adsorption is higher in batch than in open-flow column (Boekold and Van der Zee, 1992; Grohmann et al., 1995; Bajracharya et al., 1996). The reasons for this paradoxical behaviour are mainly (i) the presence of immobile water in the column, which acts as a kinetic barrier (Nkedi-Kizza et al., 1985; Maraqa et al., 1997; Plassard et al., 2000), (ii) the difference of solid/solution ratio between batch and column (O’Connor and Connolly, 1980; Voice et al., 1983; Di Toro, 1985), or (iii) the unachievement of chemical equilibrium in column if the mean residence time is significantly lower than the mean reaction time (Bilkert and Rao, 1985; Brusseau et al., 1991; Maraqa et al., 1998; Thomsen et al., 1999; Altfelder et al., 2001). The spatial chemical heterogeneities of the medium have also been invoked (Chrysikopoulos et al., 1990; Brusseau and Zachara, 1993; Wise, 1993; Fesch et al., 1998), but they can be neglected compared with the heterogeneity of the pore water velocities (Brusseau and Zachara, 1993; Johnson et al., 2003). Maraqa (2001a) investigated the adsorption of an organic compound on a sandy material in batch, open-flow column and recirculated-flow column. The distribution coefficients obtained in batch or with recircu-

Fig. 10. Comparison of two uranyl isotherms obtained by the batch or column method in a silica–goethite medium (after Gabriel et al., 1998). The authors show that the lower adsorption in batch is due to the competition between uranyl and dissolved silica, while impossible in column because of continuous flushing.
lated-flow column are similar whereas they are 30–170% higher in open-flow column. Therefore, the differences usually observed between batch and flow-through methods could not be due to the different solid/solution ratios but only to the removal of the solution. Since many systems of interest are open and dynamic in nature (solute diffusion in clays, solute transfers in soils and aquifers, particle transport in lakes or rivers...), one can think that open-flow methods are closer to these natural conditions and thus should be preferred as often as possible (Schweich et al., 1983; Sparks, 1985), taking into account the background composition of the injected solution.

4.1.3. The composition of the background solution

As indicated in Section 3.5, the ionic and molecular background of the solution is of major importance, especially when adsorption or desorption is governed by competing mechanisms such as ion exchange. If the solution is well equilibrated with the solid, the differences between experiments performed with deionised or pre-equilibrated water can be negligible. This condition can be completed for batch experiments with a solid/solution ratio high enough. However, for any other condition (batch experiment with low solid/solution ratio or flow-through experiment), the background composition of the solution must be as close as possible to what is expected or measured in natural conditions. For example, Martin-Garin et al. (2003), showed the influence of the pre-equilibration on the adsorption of Cd on calcite in stirred-flow through experiments (Fig. 11) and managed to describe the observed differences among their results and other batch data by modelling the effects of pH and Ca concentration.

4.2. Description, advantages, and disadvantages of the methods

Table 3 summarizes the main characteristics, advantages and disadvantages of each method for an appropriate purpose.

4.2.1. The batch method

The batch is far easier to use than any other method. The solid is shaken in the solution until the adsorption or desorption equilibrium is reached. Then, the remaining solute concentration is measured.

The disadvantages are numerous. The solid/solution ratio is often either too high compared with the natural conditions in rivers, lakes or seas, or too low compared with the natural conditions of porous media. Moreover, the hydrodynamic conditions of natural porous media are not met. A long term experiment with continuous shaking can lead to side reactions (Sposito, 1984, p. 113) such as the destruction of particles, which prevents the study of very slow reactions. As a consequence, the batch method is very useful as a preliminary experiment but extrapolation to porous media requires other investigations.
4.2.2. The flow-through methods

A solution that does not contain the considered reactive solute is continuously injected at the inlet of the reactor. Then, the reactive compound is (i) instantaneously injected at the inlet of the reactor (Dirac injection) or (ii) continuously injected during a time period (finite step injection) or (iii) continuously injected after a given time (infinite step injection). The outlet solution can be flushed or re-injected (Maraqa, 2001a). In addition, one can adjust the flow rate, so that the mean residence time can be chosen to be higher or close to the mean reaction time, or even lower if the reaction is not instantaneous. Thus, the kinetic dependence is easier to investigate than in the batch method.

An excellent review has been written about the relations between sorption isotherms and breakthrough curves (Schweich and Sardin, 1981) and some of the simple rules were formally established by Golden (1969). A recent review provides some other examples of relations between isotherms and breakthrough curves (Seidel-Morgenstern, 2004). In the common case of a concave isotherm, the asymmetry of the breakthrough curve is strengthened. However, it is important to remember that many other mechanisms can create asymmetry, such as (i) the presence of immobile water (e.g. Van Genuchten and Wieranga, 1976, 1977; Van Genuchten et al., 1977; Valocchi, 1985; Ma and Selim, 1997; Maraqa, 2001b), or (ii) slow adsorption or desorption kinetics (e.g. Rubin, 1983, or see Fig. 5), or (iii) preferential flowpaths (Jury and Roth, 1990; Jury and Flühler, 1992), or (iv) colloidal transport (Ryan and Elimelech, 1996; Kretzschmar et al., 1999), or (v) simply a low ratio between advection and dispersion (low Peclet number). So, the experiments must be performed in different conditions (injected concentrations, flow rates, etc.) in order to test their influence independently and to avoid erroneous conclusions. In the presence of noticeable asymmetry, the main experimental difficulty consists in measuring precisely the tail (Schweich and Sardin, 1981; Altfelder et al., 2001; Maraqa, 2001a; Pang et al., 2003). Most of the time, the recovery of the adsorption or desorption isotherm from a breakthrough curve needs to solve a system containing the transport equation of the inert tracer added to an equilibrium and/or a kinetic model of the adsorption/desorption. This mathematical issue is often complex. However, one can provide two simple qualitative rules: (i) if two adimensioned breakthrough curves of a reactive tracer made with two different injected concentrations and the same flow rate are not superimposed, it means that the isotherm is not linear; and (ii) if two adimensioned breakthrough curves of a reactive tracer made with two different flow rates and the same injected concentration are not superimposed, it means that a kinetic effect is involved. More details about the recovery of an isotherm from a column or a stirred-flow breakthrough curve are discussed in the following paragraphs.

4.2.2.1. The stirred flow-through reactor. This system is also named “stirred flow cell” or “stirred flow chamber” and was developed following the concept of the continuous-flow stirred tank (Carski and Sparks, 1985; Rimstidt and Dove, 1986; Randle and Hartmann, 1987; Miller et al., 1989a; Schnabel and Fitting, 1989; Seyfried et al., 1989; Sparks, 1989; Zhang and Sparks, 1993) that is widely used in engineering and industry. It consists in injecting

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Table 3
Main characteristics of experimental methods for the measurement of adsorption/desorption isotherms and kinetics

<table>
<thead>
<tr>
<th>Method</th>
<th>Solid/solution ratio</th>
<th>Adsorption measurement</th>
<th>Desorption measurement</th>
<th>Inert tracer</th>
<th>Main advantage/Main disadvantage</th>
<th>Appropriate purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch</td>
<td>Chosen (&lt;1 kg L⁻¹)</td>
<td>Easy</td>
<td>Difficult (step by step)</td>
<td>No</td>
<td>Easy-to-use/unrealistic for porous media</td>
<td>Preliminary measurements</td>
</tr>
<tr>
<td>Stirred flow cell</td>
<td>Chosen (&lt;1 kg L⁻¹)</td>
<td>Easy</td>
<td>Easy</td>
<td>Possibly no</td>
<td>Flow-through with chosen solid/solution ratio</td>
<td>Reaction kinetics, release measurement</td>
</tr>
<tr>
<td>Repacked column</td>
<td>High (≥ bulk density)</td>
<td>Easy</td>
<td>Easy</td>
<td>Yes</td>
<td>Solid/solution ratio of porous media/structure destroyed</td>
<td>Transfer in poorly structured porous media</td>
</tr>
<tr>
<td>Zero-length column</td>
<td>High (≥ bulk density)</td>
<td>Difficult (or fast reaction)</td>
<td>Easy</td>
<td>Possibly no</td>
<td>Negligible dispersion/low reaction time</td>
<td>Kinetics of release</td>
</tr>
</tbody>
</table>

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a step of the reactive tracer through a stirred cell containing a known mass of the solid in contact with the solution, and then comparing the breakthrough curves of the reactive solute with that of an inert tracer.

For a perfect stirred flow-through reactor, the solution composition is assumed to be homogeneous within the reactor and equals the outlet one. The breakthrough curve of an inert tracer following a step injection from $C = 0$ to $C_0$ (Fig. 12b) is given by Eq. (26) (Denbigh, 1944; Villermaux, 1993)

$$C = C_0 \left[ 1 - \exp \left( -\frac{\phi}{V_0} (t - t_0) \right) \right]$$  

(26)

where $t$ is time, $t_0$ is the instant when the tracer is injected, $\phi$ (L s$^{-1}$) represents the flow rate and $V_0$ (L) is the volume of the solution inside the reactor (i.e. the volume of the reactor minus the volume of the solid). The ratio $V_0/\phi$ defines the mean residence time in the reactor for an inert tracer. For the desorption stage (switching back the injected concentration to zero), the breakthrough curve of an inert tracer (Fig. 12b) is given by Eq. (27) (Denbigh, 1944; Villermaux, 1993)

$$C = C_0 \exp \left( -\frac{\phi}{V_0} (t - t_1) \right)$$  

(27)

where $t_1$ is the instant when the injection of the tracer is stopped.

Knowing these two equations, it is often not necessary to measure the breakthrough curve of an inert tracer: most of the time, there is no difference

---

**Fig. 12.** Adsorption kinetics of Co on a soil measured (a) in batch and (b) in stirred flow-through reactor with the same background solution (from Limousin, 2006). The batch method indicated a fast adsorption, but it prevented from concluding to a slow reaction because of long-term side effects, such as particle disrupting. On the contrary, the stirred-flow through method used with two different mean water residence times confirmed the existence of slow reactions.
between the computed and measured breakthrough curve when the solid is well mixed. For a reactive solute, the breakthrough curve deviates from that predicted in Eq. (26) (resp. (27)) and the amount of adsorbed (resp. desorbed) solute is given by the surface area separating the breakthrough curve of the reactive solute and of the inert tracer (Fig. 13). Modelling the breakthrough curve of a reactive solute consists in solving a system of several equations: Eq. (26) or (27) coupled with an equilibrium or a kinetic model (e.g. Bar-Tal et al., 1990 for some analytical solutions taking into account a kinetic dependence). The difference between the surface area of the adsorption stage and the surface area of the desorption stage provides the amount of reactive solute which was pseudo-irreversibly adsorbed (since the quantity of adsorbed solute can be negligible compared with the total injected quantity, this type of mass balance is often more appropriate to know the amount of pseudo-irreversibly adsorbed compound than the difference between the total injected mass and the total recovered mass). Without coupling the chemical-transport model, it is possible to construct the isotherm by discretizing the

![Same breakthrough curve from a stirred flow-through experiment](image)

**Fig. 13.** Construction of the adsorption isotherm from the breakthrough curve of an inert and a reactive tracer obtained with the stirred flow-through reactor, assuming that the reaction is instantaneous. The relation between the hatched surface area $A_t$ of the breakthrough curve and the solid concentration $Q_t$ is given by: $Q_t = \frac{\text{flow rate}}{\text{solid mass}} \times A_t = \frac{\text{flow rate}}{\text{solid mass}} \left( \int_{t_0}^{t_1} C_{\text{inert tracer}} \, dt - \int_{t_0}^{t_1} C_{\text{reactive compound}} \, dt \right)$. The desorption isotherm is obtained by the same procedure with the desorption stage of the breakthrough curve.
studied concentration range (from \( C = 0 \) to \( C_{0} \)) into \( n \) concentration intervals (the \( i \)th interval being from \( C = 0 \) to \( C_{i} \)). Then, the corresponding adsorbed fraction between \( C = 0 \) and \( C_{i} \) is calculated using the surface area between the breakthrough curves of the inert and reactive tracers inside this interval (Fig. 13). Each of these calculations provides one point \( (C_{i}, Q_{i}) \) of the isotherm. This method has the advantage of avoiding any model assumption and requiring only one breakthrough curve to construct a complete isotherm. However, several issues remain. First, a precise isotherm requires a high number of points. But the greater the concentration intervals are, the smaller is the precision on each surface area between the breakthrough curves of the inert and reactive tracers. In addition, the greater the non-linearity of the isotherm, the smaller the difference between two intervals must be in order to have good precision, which leads to the strong assumption that the reaction must be considered instantaneous not only compared to the mean residence time of the inert tracer, but also to the time corresponding to each concentration interval. These limits in the precision of this method explain why the coupling-transport models are often preferred. Martin-Garin et al. (2003) showed, however, the feasibility of constructing the isotherm by performing several breakthrough experiments with different concentrations, each of them providing only one point of the isotherm by the total mass balance between the reactive and the inert tracer, instead of several points for one breakthrough curve. This method is valid only if the isotherm can be considered linear in the concentration range of each breakthrough curve, but it provided good consistency with other batch data (Fig. 11).

The two main disadvantages often pointed out in the literature are (i) sealing, which prevents conducting long experiments and (ii) the magnetic stir bar placed inside the cell that progressively destroys the solid particles (Deitsch and Smith, 1995; Pignatelatto, 2000). These two problems can be avoided (i) by reversing the sense of the flow inside the cell intermittently without reversing the complete circuit (Heyse et al., 1997; Barthès et al., 2004) to prevent the filters from being sealed, and (ii) by using an external system that shakes the cell instead of placing a stir bar inside (Furrer et al., 1993; Zyset and Schindler, 1996).

In conclusion, the stirred flow-through reactor is much more appropriate than the batch method to study the release stage (e.g. Grolimund et al., 1995; Martin-Garin et al., 2003; Szenknect et al., 2005), and provides satisfactory results to predict the breakthrough curves obtained with a repacked column (Szenknect et al., 2005). Moreover, the flow rate (and thus the mean contact time of the solute with the solid) can be adjusted to measure the influence of chemical kinetics (e.g. Bar-Tal et al., 1990; Eick et al., 1990; Nagy and Lasaga, 1992; Van Capellen and Qiu, 1997a,b; Martin-Garin et al., 2003), as shown in Fig. 13 (Limousin, 2006).

4.2.2.2. The repacked column. This column is packed with the solid particles, and the solution goes through. An example of typical breakthrough curves of inert and reactive tracers is shown in Fig. 5 (Limousin, 2006). Like the stirred flow-through reactor, this method has the advantage of being an open-flow method. So, the chemical kinetics and the release stage can be studied more easily than with the batch method (Sparks et al., 1980; Sparks and Rechcigl, 1982). Moreover, the solid/solution ratio is representative of natural porous media. Furthermore, the experiments can be run either in water saturated or unsaturated conditions (Plassard et al., 2000; Porro et al., 2000). However this flow-through method has some disadvantages. For example, the duration of the experiment can be long, especially for strongly adsorbed solutes or in the case of compacted of unsaturated clay materials with low hydraulic conductivity.

The main disadvantage of this technique is that the system is not perfectly mixed and the breakthrough curve of the reactive compound also contains the hydrodynamic dispersion of the medium. So, a comparison with an inert tracer is unavoidable to know how chemical reactions are involved. Taking into account hydrodynamic processes adds to the complexity of the problem and, contrary to the stirred-flow through method, it prevents constructing the isotherm without choosing a chemical model. Some analytical solutions for the case of negligible dispersion (De Vault, 1943; Glueckauf, 1945) have shown their limitations because of the dispersion or of the presence of immobile water (Glueckauf and Coates, 1947; Merriam and Thomas, 1956). Thus, fitting a coupling chemical-transport model to the breakthrough curve and then verifying the parameters of the model in different conditions remains the simplest method to obtain information on the adsorption or desorption isotherm. Moreover, several numerical models have been developed to calculate the adsorption or
desorption isotherm from dispersive breakthrough curves (e.g. Schweich et al., 1983; Kool et al., 1989; Griffioen et al., 1992).

4.2.2.3. The zero-length column. An original method has been proposed to nullify the effects of the porous network (hydrodynamic dispersion, preferential pathways, immobile water, etc.). The column is thin enough so that its dispersivity is close to zero and the breakthrough curve is only sensitive to the chemical properties of the medium (Eic and Ruthven, 1988; Ruthven and Eic, 1988).

This method is particularly suited to highly adsorbed compounds or to desorption studies (especially for already polluted porous media). Compared with classical column methods, this technique can be performed without an inert tracer. However, the length of the column must be thin enough and the flow rate must be high enough to overcome the dispersive effects. Thus, this method is often not suitable for adsorption measurements.

5. Conclusion

The sorption isotherm is a common approach to describe a great diversity of retention/release phenomena. This is very useful and often unavoidable to understand and predict the mobility of sorbing substances in the environment. However, this approach is macroscopic and empirical in nature, thus not saying, by itself, anything on the complicated mechanisms involved. In particular, it is important to verify if thermodynamic equilibrium is reached within the reaction- (or residence-) time, both for the retention and for the release stage of the compound. Otherwise kinetic experiments must be considered.

Since the isotherm is not an intrinsic property of the substance/solid couple, the measurement method has a great influence on the results. Thus, it must be chosen carefully and always described with the results in detail.

Other methods allow the investigation of the retention microscopically, particularly with spectroscopic and microscopic tools. They have provided a new efficient way to verify several assumptions used in isotherm interpretations on the solid structure and retention/release mechanisms, thus leading to more confidence in structure-based and mechanism-based complexation models. These models should replace the traditional “K_d” approach. On the other hand, the increasing power of computers makes possible not only improving mechanistic models of speciation, but also running “Molecular Dynamic Experiments”. However, natural media are such complicated mixtures of numerous mineral and organic compounds that empirical approaches such as the “sorption isotherm” will be still used for a long time.

Acknowledgements

The authors acknowledge partial funding from “Electricité de France” and French Atomic Energy Commission. We thank all the reviewers who participated in the improvement of this paper.

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