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Determining rate coefficients for ion adsorption at the solid/water interface. Better from desorption rate than from adsorption rate

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Abstract

One of the most common approaches in the adsorption kinetic literature is to compare the fitting performance of several empirical or non-empirical equations (pseudo-first order, pseudo-second order, Elovich, parabolic diffusion, etc.) with the aim of selecting the equation that best describes the experimental data. This is normally a futile fitting exercise that leads to the determination of ambiguous rate parameters, without providing insights into the behaviour of the studied system. A more realistic approach is to treat it as a combination of mass transport and chemical reaction under controlled conditions, and thus actual adsorption-desorption rate parameters are readily estimated. This article applies a simple and realistic physicochemical model to describe and understand the adsorption-desorption kinetics of ions at the solid/water interface. The model is applied to an ATR-FTIR study of phosphate adsorption-desorption on goethite, which is a very well-known and reference system, ideal for testing the performance of a physicochemical treatment that combines transport and reaction. Always the same phosphate species (monodentate mononuclear protonated) was present at the goethite surface during adsorption-desorption. There was an excellent agreement between theory and experiments at a variety of phosphate concentration and surface coverages for adsorption kinetics, desorption kinetics and equilibrium situations, employing just one set of rate coefficients. The use of rate vs adsorption curves permitted easily to detect conditions of transport- and reaction-controlled kinetics. The phosphate-goethite system is a fast-adsorbing/slow-desorbing system, with an adsorption rate constant k_a^o=1.26×10^3 s^{-1} and a desorption rate constant k_d=1.66×10^{-5} s^{-1}. Therefore, adsorption was transport-controlled and desorption was reaction-controlled. The half-life of the desorption reaction is 41700 s (11.6 h) but for adsorption it would take only a few seconds in absence of transport control. For this kind of systems, which are ubiquitous in nature and technological

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processes, it is easier to determine rate constants from desorption than from adsorption experiments.

Key Words: adsorption kinetics; oxide-water interface; surface complexes; phosphate desorption.

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Introduction

Many environmental and technological processes are governed or influenced by adsorption-desorption reactions at the solid-water interface. Situations under equilibrium are usually described by several adsorption models, with rather simple equations, such as the Langmuir isotherm (1),(2), or with more complicated combinations of equations, such as surface complexation models (3),(4), that describe adsorption of ions and complexing molecules at charged solid/liquid interfaces. Dynamic situations, where the kinetics of adsorption and desorption needs to be modelled, are usually more difficult to undertake, and thus they are less investigated with proper detail, even though adsorption kinetics is of paramount significance in environment and technology.

In general, the adsorption process from a homogenised or well-stirred bulk solution results in a combination of mass transport, where the adsorbing species is transported to the surface, and a chemical (or physical) reaction, where the species that arrived to the surface by transport stablishes the chemical (or physical) bond with surface groups. Simple kinetic equations or models do not consider the combination of mass transport and reaction, neglecting one of them when treating adsorption kinetics(1),(2),(5). This simplified treatment leads to the determination of ambiguous rate parameters from data fitting because they include the effects of the neglected process. As a result, the so-obtained parameters can only be applied to conditions that exactly match the measuring conditions and cannot be safely translated and used in a different situation.

One of the most common approaches in the adsorption kinetic literature is to compare the fitting performance of several empirical or non-empirical equations (pseudo-first order, pseudo-second order, Elovich, parabolic diffusion, etc.) with the aim of selecting the equation that best describes the experimental data and obtaining the rate constant or other parameters that appear in it. As indicated above, the obtained rate

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constants or parameters are ambiguous, with low physical significance, or even meaningless. Thus, a whole adsorption desorption kinetic study may become just a fitting exercise, without providing insights into the behaviour of the studied system, obstructing our understanding of the mechanisms that govern adsorption-desorption at the solid/liquid interfaces (6).

In spite of the alleged difficulties of kinetic treatments for adsorption-desorption reactions, there are systems where the dynamics can be undertaken, in principle, without complications. This is the case of flow systems with ATR-FTIR detection of the adsorbed species (7). On one side, the flow system allows flowing always fresh solution with a constant and well controlled adsorbate concentration. On the other side, infrared spectroscopy can selectively detect the adsorbed species and monitor the change of its concentration during a kinetic run, allowing for a precise identification and quantification of the product of the adsorption reaction (8),(9). With the right treatment of the system and the obtained data, it is possible to identify the conditions where mass transport controls the kinetics, or where reaction controls it, allowing for a proper evaluation of the rate parameters, such as the attachment rate constant, k_a, or the detachment rate constant, k_d (see below).

The overwhelming majority of adsorption-desorption studies rely on adsorption kinetic data to find the rate parameters (10). Only very few studies used desorption kinetic information for that purpose (11). Since any adsorption system is a dynamic system, adsorption always occurs simultaneously with desorption, and what is actually measured is the net rate of the process. Therefore, the rate parameters can, in principle, be obtained from adsorption kinetic runs, desorption kinetic runs or both. In addition, as mass transport is always connected to reaction, there may be situations where transport affects considerably the adsorption rate, not influencing the desorption rate. Under these

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conditions, measuring desorption kinetics would be much more useful than measuring adsorption kinetics.

The aim of this paper is to use a very simple but realistic physicochemical model that combines mass transport and reaction at the surface to describe simultaneously adsorption and desorption kinetics at the solid/water interface as measured in an ATR-FTIR flow cell. The treatment is applied to the adsorption-desorption kinetics of phosphate on goethite in aqueous media. Due to its environmental importance, the system phosphate-goethite has become a model system and there is abundant information about adsorption-desorption under very different conditions (3)(9)(12)(13)(14). Such a highly studied system is ideal to test this simple treatment, and to check whether adsorption kinetic or desorption kinetic runs are better for determining the rate parameters.

Experimental

Chemicals. All chemicals were of analytical grade and used as received. Double distilled water was used for the preparation of solutions.

Synthesis and characterization of goethite. The goethite used in this study was an aliquot of a previously prepared and investigated sample (15). It was prepared following a procedure similar to that described by Atkinson et al. (16). A 5M NaOH solution was added dropwise to a 0.1 M $Fe(NO_3)_3.9H_2O$ solution until the final pH was 12. This reaction led to the formation of a ferrihydrite dispersion, which was then aged at 60ºC during 3 days in a capped teflon bottle, in order to produce goethite crystallization. The obtained goethite particles were filtered and washed with CO_2-free water until the conductivity of the supernatant was lower than 10 μS cm^{-1}. The washed solid was stored as a stock suspension (9.63 gL^{-1}) at pH 4.5 in water. Its N_2-BET surface area was 89.7

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m^2g^{-1} and its isoelectric point (IEP) was 8.6. The X-ray diffraction pattern and IR spectrum were typical of pure goethite.

Adsorption isotherm. An adsorption isotherm at pH 7.0 was obtained by batch equilibration using 15-mL polypropylene centrifuge tubes, using 0.1M NaCl as supporting electrolyte. Each tube contained 0.7 mL of the stock goethite suspension and 10 mL of a phosphate solution of known concentration. The tubes were then shaken for 6 h (enough to achieve equilibration) with an end-over-end rotator and then the concentration of phosphate remaining in the supernatant solution was quantified. Adsorbed phosphate was calculated from the difference between the initial and final concentrations. Quantification of phosphate in solution was done by UV–VIS spectrophotometry using the molybdenum blue method (17), recording the spectra in the 200–1000 nm wavelength range and using the absorbance at 880 nm for calculation. Calibration curves were constructed with phosphate solutions prepared at pH 7.0 in 0.1 M NaCl. An Agilent 8453 UV-Vis diode array spectrophotometer equipped with a 1-cm Hellma quartz cell was used for spectral readings.

ATR-FTIR adsorption-desorption kinetics. Phosphate adsorption-desorption kinetics was monitored by ATR-FTIR spectroscopy using a Thermo Fisher Scientific ARK flow cell containing a ZnSe crystal (area: 10 x 72 mm, incident angle: 45º, total reflections: 12) as internal reflection element. A schematic representation of the flow cell used for the measurements is shown in Fig. 1. The goethite film was made by pouring 210 µL of the stock goethite dispersion over the ZnSe crystal and letting it dry on air. Once the film was formed, the solution of interest was flown from a reservoir (capped vase with a stirred solution of controlled pH and temperature, under nitrogen bubbling) to the cell with a

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Gilson Minipuls 8 peristaltic pump at a flow rate of 3.3 mL min^{-1}. An open flow system was used in all cases, with fresh solution always flowing through the cell, being discarded by the outlet tubing. The supporting electrolyte was 0.1M NaCl at pH 7.0 in all cases, and the working temperature was 24±2 ºC. Each recorded spectrum was the average of 128 scans, with a spectral resolution of 16 cm^{-1}.

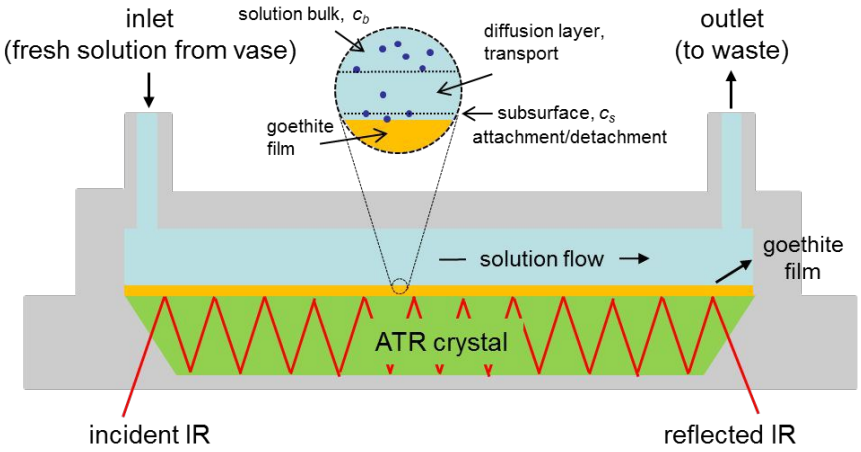

Fig. 1. Scheme of the flow cell used in the experiments.

A typical phosphate adsorption-desorption experiment started by flowing the supporting electrolyte through the cell followed by the acquisition of a blank spectrum. After that, a phosphate solution of the desired concentration (pH 7.0, in 0.1M NaCl) was flown to produce phosphate adsorption on goethite, registering IR spectra as a function of time until the intensity of the signal levelled off (around 3 h for the lowest phosphate concentration, 3×10^{-6} M, and around 1 h for the highest phosphate concentration, 3×10^{-4} M). Once the last spectrum was acquired, the supporting electrolyte was again flown, in order to induce desorption at the same pH, and IR spectra were registered as a function of time to monitor the desorption kinetics during 1 h. Longer desorption times did not ensure a stable baseline. A fresh goethite film was prepared for each adsorption-desorption run. Calibration of the equipment was performed with the aid of the adsorption

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isotherm under the same working conditions, matching the absorbance at long reaction times with the adsorbed amount obtained from the isotherm.

Theoretical background

The adsorption-desorption kinetics at the solid/liquid interface results from the combination of transport and attachment-detachment of the reacting ions or molecules. For practical purposes, it is convenient to express the concentration, c', as a dimensionless [-] quantity, dividing the actual molar concentration, c, by its standard state, c^o = 1M. Therefore, $c' = {}^{c}/_{c^o}$ and thus, for calculations, c' has the same magnitude than the molar concentration but no units. This procedure allows to have rate parameters with proper units. Therefore, the transport rate, J_t [s^{-1}], can be expressed as a function of the concentration gradient in the diffusion layer near the surface (Fig. 1) as follows

$$J_t = k_t(c'_b - c'_s) \quad (1)$$

Where k_t [s^{-1}] is a transport rate coefficient, c'_b, is the concentration of the adsorbing species in the bulk solution and c'_s is its concentration on a subsurface layer, adjacent to the surface. Once located in the subsurface layer, the adsorbing species is already "touching" the surface, and it just needs to become bonded or attached to the surface groups. Thus, the species will attach the surface with an attachment rate coefficient k_a [s^{-1}] and will detach from the surface with a detachment rate coefficient k_d [s^{-1}], resulting in an attachment/detachment (reaction) rate, $\frac{d\theta}{dt}$ [s^{-1}], that is given by forward and backward terms as follows:

$$\frac{d\theta}{dt} = k_a c'_s(1-\theta) - k_d\theta \quad (2)$$

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Where θ is the surface coverage, $\theta = \frac{\Gamma}{\Gamma_m}$, Γ [µmol m^{-2}] is the adsorbed amount per unit area and Γ_m [µmol m^{-2}] its maximum value, obtained at surface saturation. The rate in terms of adsorbed amount, $\frac{d\Gamma}{dt}$ [µmol m^{-2} s^{-1}], can be easily obtained from

$$\frac{d\Gamma}{dt} = \frac{d\theta}{dt}\Gamma_m \quad (3)$$

In a steady-state situation the transport rate should equal the reaction rate and thus the following expression for c'_s can be found from the combination of Eq. 1 and 2:

$$c'_s = \frac{k_d\theta + k_t c'_b}{k_a(1-\theta) + k_t} \quad (4)$$

This expression can be substituted in Eq. 2 to give the general adsorption-desorption equation where transport and attachment/detachment are combined

$$\frac{d\theta}{dt} = \frac{k_t k_a(1-\theta)c'_b - k_t k_d\theta}{k_a(1-\theta) + k_t} \quad (5)$$

This Eq. can be evaluated under equilibrium conditions. Knowing that at equilibrium $\frac{d\theta}{dt} = 0$ and c'_b=c'_{eq}, where c'_{eq} is the equilibrium concentration, Eq. 5 leads to:

$$\frac{\theta}{(1-\theta)} = \frac{k_a}{k_d}c'_{eq} \quad (6)$$

Which is the adsorption isotherm, relating θ with c'_{eq}.

Using the adsorption isotherm, and substituting $k_d\theta$ in Eq. 5 by $k_a(1-\theta)c'_{eq}$, another form of eq. 5 is obtained:

$$\frac{d\theta}{dt} = \frac{k_t k_a(1-\theta)}{k_a(1-\theta) + k_t}\left(c'_b - c'_{eq}\right) \quad (7)$$

Where c'_{eq} corresponds to the θ specified in the equation. Equations 5 and 7 are equivalent and can be used indistinctively. They represent the general equation that combines transport and reaction for calculation of the adsorption-desorption rate at a given c'_b, provided the values or expressions for k_t, k_a, k_d and Γ_m are known. If, for example, $c'_b > c'_{eq}$, the rate is positive ($\frac{d\theta}{dt} > 0$) and thus net adsorption takes place and k_t, k_a, k_d can be

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obtained from an adsorption kinetic run. On the contrary, if $c'_b < c'_{eq}$ the rate is negative ($\frac{d\theta}{dt} < 0$) and thus net desorption takes place and k_t, k_a, k_d can be obtained from a desorption kinetic run. Different special situations can be deduced starting from the general equations 5 and 7, such as those found under the conditions of transport control, reaction control, initial adsorption rate $\left(\frac{d\theta}{dt}\right)_{i,ads}$, initial desorption rate $\left(\frac{d\theta}{dt}\right)_{i,des}$, etc. These different situations and their corresponding equations are listed in Table 1.

Table 1. Equations of the model used in calculations*

Condition	General equation	Initial adsorption (Γ=0, c'_{eq}=0)	Initial desorption (Γ= Γ_i, c'_b=0)
mixed transport and reaction	$\frac{d\theta}{dt} = \frac{k_t k_a (1-\theta) c'_b - k_t k_d \theta}{k_a(1-\theta) + k_t}$ (5) $\frac{d\theta}{dt} = \frac{k_t k_a (1-\theta)}{k_a(1-\theta) + k_t}\left(c'_b - c'_{eq}\right)$ (7)	$\left(\frac{d\theta}{dt}\right)_{i,ads} = \frac{k_t k_a}{k_a + k_t} c'_b$ (10)	$\left(\frac{d\theta}{dt}\right)_{i,d} = -\frac{k_t k_d \theta_i}{k_a(1-\theta_i) + k_t}$ (13)
transport control ($k_a (1-\theta) \gg k_t$)	$\frac{d\theta}{dt} = k_t\left(c'_b - c'_{eq}\right)$ (8)	$\left(\frac{d\theta}{dt}\right)_{i,ads} = k_t c'_b$ (11)	$\left(\frac{d\theta}{dt}\right)_{i,d} = -\frac{k_t k_d \theta_i}{k_a(1-\theta_i)}$ (14)
reaction control ($k_a (1-\theta) \ll k_t$)	$\frac{d\theta}{dt} = k_a(1-\theta)\left(c'_b - c'_{eq}\right)$ (9)	$\left(\frac{d\theta}{dt}\right)_{i,ads} = k_a c'_b$ (12)	$\left(\frac{d\theta}{dt}\right)_{i,d} = -k_d \theta_i$ (15)

* Equations 5 and 7 are the general equations already indicated in the text, and equations 8 to 15 are derived from them under special conditions of transport control, reaction control, initial adsorption or initial desorption, as indicated in the table.

In all equations k_a is a constant for Langmuir kinetics and $k_a = k_a^o \exp(-b\theta)$ for FFG kinetics

Γ_i, θ_i: adsorbed amount and surface coverage at the beginning of the desorption experiment

c'_{eq}: equilibrium concentration that corresponds to the specified θ

The equations written so far are rather general. By introducing the appropriate definition of the rate coefficient k_a, for instance, the kinetic models related to Langmuir or Frumkin-Fowler-Guggenheim (FFG) adsorption isotherms are obtained. If k_a is considered to be a constant, independent on the surface coverage, eq. 6 is directly the Langmuir isotherm, with $\frac{k_a}{k_d} = K_L$, the Langmuir constant. If on the contrary k_a is considered to vary with the surface coverage as $k_a = k_a^o \exp(-b\theta)$, eq. 6 becomes

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$$\frac{\theta}{(1-\theta)} = \frac{k_a^o \exp(-b\theta)}{k_d} c'_{eq} \quad (16)$$

Which is the FFG isotherm where k_a^o is a constant, $\frac{k_a^o}{k_d} = K_{FFG}$ is the FFG constant and b is the lateral interaction parameter (18).

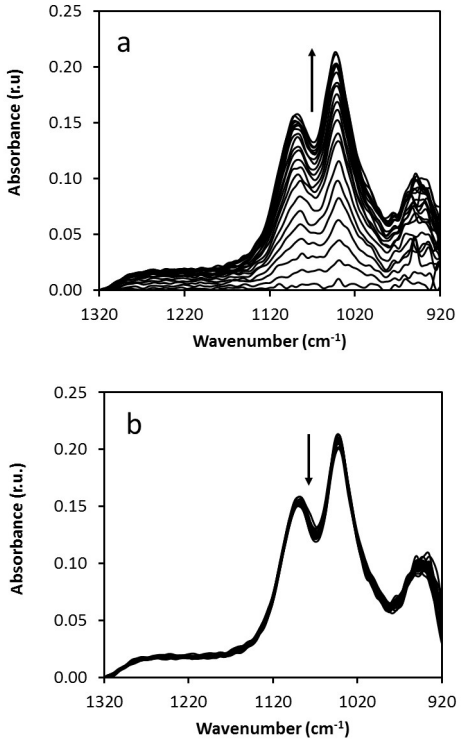

Fig. 2. ATR-FTIR spectra obtained during phosphate a) adsorption and b) desorption experiments. pH 7, c'_b =3×10^{-6}. Arrows indicate increasing time.

Results and Discussion

Figure 2 shows, as an example, the ATR-FTIR spectra obtained during adsorption-desorption kinetic measurements at pH 7.0 for a phosphate concentration 3×10^{-6} M (c'_b =3×10^{-6}). When the phosphate solution flowed in the system, the absorbance increased as time increased, indicating that adsorption was taking place. The reverse phenomenon, although less noticeable, was observed when the film was washed by flowing electrolyte at the same pH, indicating desorption. The spectra showed three main absorption bands, at 935, 1041 and 1091 cm^{-1}, characteristic of an inner-sphere surface complex, the

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monodentate mononuclear protonated species (9). The spectral shape did not change during adsorption and desorption, meaning that always the same species was present at the goethite surface. The behaviour shown in Fig. 2 for phosphate concentration c'_b=3×10^{-6} was observed for all concentrations investigated. The only difference was in the adsorption rate, which increased by increasing c'_b (see below).

Figure 3a shows the Γ vs. t curve for the data corresponding to the adsorption-desorption experiment in Figure 2, whereas Figure 3b shows the phosphate adsorption isotherm. Γ vs. t curves were obtained by numerical integration (rectangle rule) of the general eq. 5, and the isotherm was calculated using eq. 16. In both figures experimental data (symbols) are compared to model calculations (lines, almost not seen because they are hidden by symbols) obtained with parameters listed in Table 2. This only set of parameters, as will be shown throughout this work, led to a very good simultaneous fit of the adsorption isotherm, the adsorption kinetics and the desorption kinetics, under all investigated conditions, giving confidence to the simple but very realistic model used here. The adsorption using c'_b=3×10^{-6} was relatively slow. Γ varied linearly with t in the initial part of the curve (Figure 3b), up to around 2000 s, corresponding to Γ values of around 0.5 μmol m^{-2}. Many data points could be collected under this linear regime, guaranteeing a proper measurement of the initial adsorption rate from the initial slope of Γ vs t. The desorption part of the curve also showed good linearity, with many data points, allowing also an appropriate measurement of the initial desorption rate. Even though reliable initial adsorption and desorption rates could be obtained under the working conditions, the meaning of these rates is vague without a clear visualization of the processes (transport, reaction, or both) controlling the adsorption.

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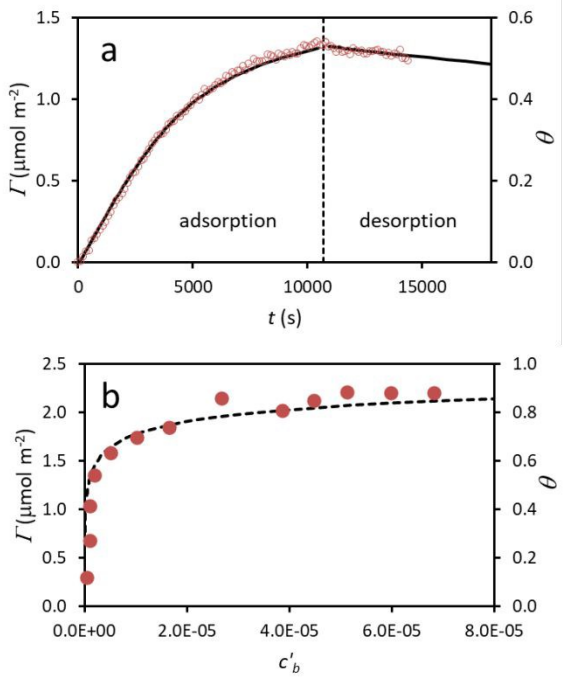

Fig. 3. a) Adsorption-desorption kinetic curves for data in Fig. 2, pH 7, c'_b=3×10^{-6}. Symbols correspond to experimental points and lines correspond to model calculations (general equation 5/7, numerical integration, rectangle rule) with parameters from Table 2. b) Adsorption isotherm of phosphate on goethite at pH 7. Symbols correspond to experimental points and lines correspond to model calculations (FFG isotherm, equation 16) with parameters from Table 2.

Table 2. Parameters of the model used in calculations*

Parameter	
k_a^o (s^{-1})	1.26×10^3
k_d (s^{-1})	1.66×10^{-5}
k_t (s^{-1})	3.54×10^1
b	8.07
Γ_m (μmol m^{-2})	2.50

* FFG kinetics was used in calculations with $k_a = k_a^o \exp(-b\theta)$

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Figure 4 shows the experimental data obtained during adsorption experiments in terms of rate vs. adsorption curves ($\frac{d\Gamma}{dt}$ vs. Γ curves). The rate was calculated from adsorption kinetic curves as $\Delta\Gamma/\Delta t$ for each pair of adjacent data points, applying media average smoothing to avoid excessive scattering of data. $\frac{d\Gamma}{dt}$ vs. Γ curves are very instructive because they allow analysing the progress of the rate as the surface is becoming populated by the adsorbed species and also permit the comparison of experimental rates with theoretical rates controlled either by transport or by reaction. Data in Figure 4 cover the full range of adsorption investigated, from c_b'=3×10^{-6} to c_b'=3×10^{-4}, and very good fitting was obtained under all these conditions with the parameters of Table 2. Figure 4a corresponds to the already analysed data in Figures 2 and 3. It is very clear for c_b'=3×10^{-6} that transport was much slower than attachment at the beginning of the reaction, and thus the process was transport-controlled at Γ<0.5 μmol m^{-2}. Only when Γ was relatively high (Γ>1.2 μmol m^{-2}), close to equilibrium values, the adsorption was reaction-controlled. Therefore, even though the initial adsorption rate could be properly measured, its value gives no information on rate coefficients k_a or k_d, because at the beginning the process is under transport control; only k_t could be obtained from the initial adsorption rate, with the use of eq. 11.

Figure 4 indicates that the adsorption became faster as the phosphate concentration increased. The initial adsorption rate was 2.5×10^{-4} μmol m^{-2} s^{-1} at c_b'=3×10^{-6}, 2.5×10^{-3} μmol m^{-2} s^{-1} at c_b'=3×10^{-5} and around 7.0×10^{-2} μmol m^{-2} s^{-1} at c_b'=1×10^{-4}. At c_b'=3×10^{-4} (Fig. 4d), which was the highest c_b' used, the adsorption was so fast that almost no data could be acquired at low Γ values and the initial adsorption rate could not be well measured. This is an important experimental disadvantage of relatively fast-adsorbing systems, where the scarcity of data makes very difficult to measure properly the initial adsorption rate under certain conditions. A second disadvantage of these fast systems is

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that they easily become transport-controlled, as it occurs in all cases of Figure 4. Therefore, even assuming that the initial adsorption rate could be measured, the determination of the rate coefficients k_a and k_d is not possible.

Measuring and reporting adsorption rates is a very common practice in the literature and it is customary to extract rate coefficients from them (13)(19)(20)(21). As it can be seen with Figure 4, this practice can lead to misinterpretation of data if there is no information on whether transport or reaction is controlling the rate. The case analysed here, for example, corresponds to a relatively fast-adsorbing system, where the attachment is faster than transport. Therefore, besides resulting difficult to measure the adsorption rate under certain conditions, the process is normally controlled by transport, and thus attachment coefficients cannot be accessed from initial adsorption rates. The fitting of the full adsorption kinetic curve is needed for that purpose.

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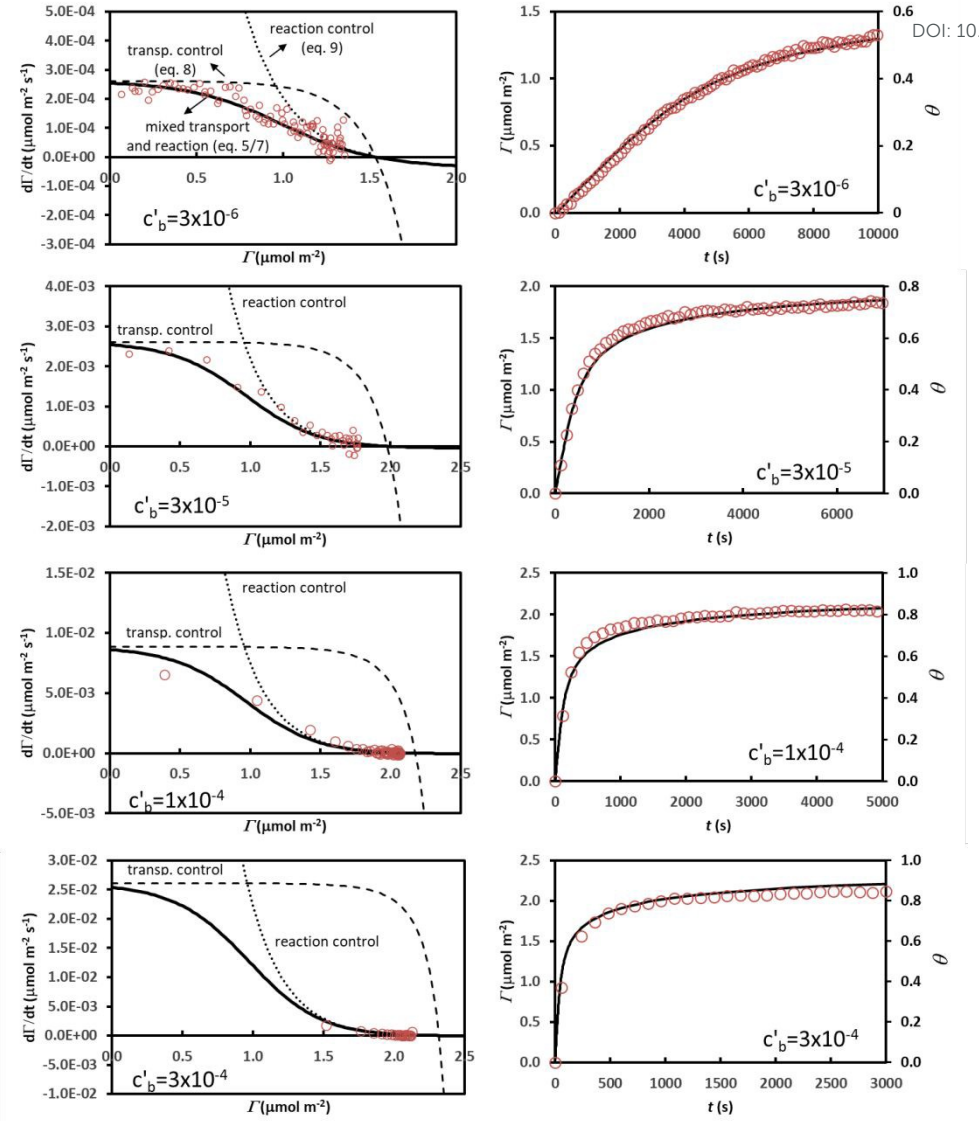

Fig. 4. Adsorption experiments. Rate vs Γ curves and adsorption kinetic curves for the investigated concentrations of phosphate. In all cases symbols correspond to experimental points and lines correspond to model calculations with parameters in Table 2. Γ vs. t curves were obtained by numerical integration (rectangle rule) of the general eq. 5.

Figure 5 shows the $\frac{d\Gamma}{dt}$ vs. Γ and the Γ vs. t curves for desorption data. Experimental data are again compared to model calculations obtained with parameters listed in Table 2. Good linearity in the Γ vs. t curves was obtained, allowing for an appropriate determination of the initial desorption rates, which varied from -2×10^{-5} μmol m^{-2} s^{-1} to -4×10^{-5} μmol m^{-2} s^{-1} (negative values indicating desorption). This is a relatively slow-

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desorbing system, the desorption process was always controlled by reaction (detachment), as can be deduced from the comparison of experimental and theoretical rates in Figure 5. It is so slow, that Γ decreased minimally in the time measured, and thus rate data could be gathered for a small range of Γ, as can be seen in the left-hand side panels of Fig. 5. In spite of this, the fact that desorption was reaction-controlled allowed for a very reliable determination of k_d from the initial desorption rates (see Eq. 15). In combination with the adsorption isotherm, it permits also to obtain k_a through the equilibrium adsorption constant.

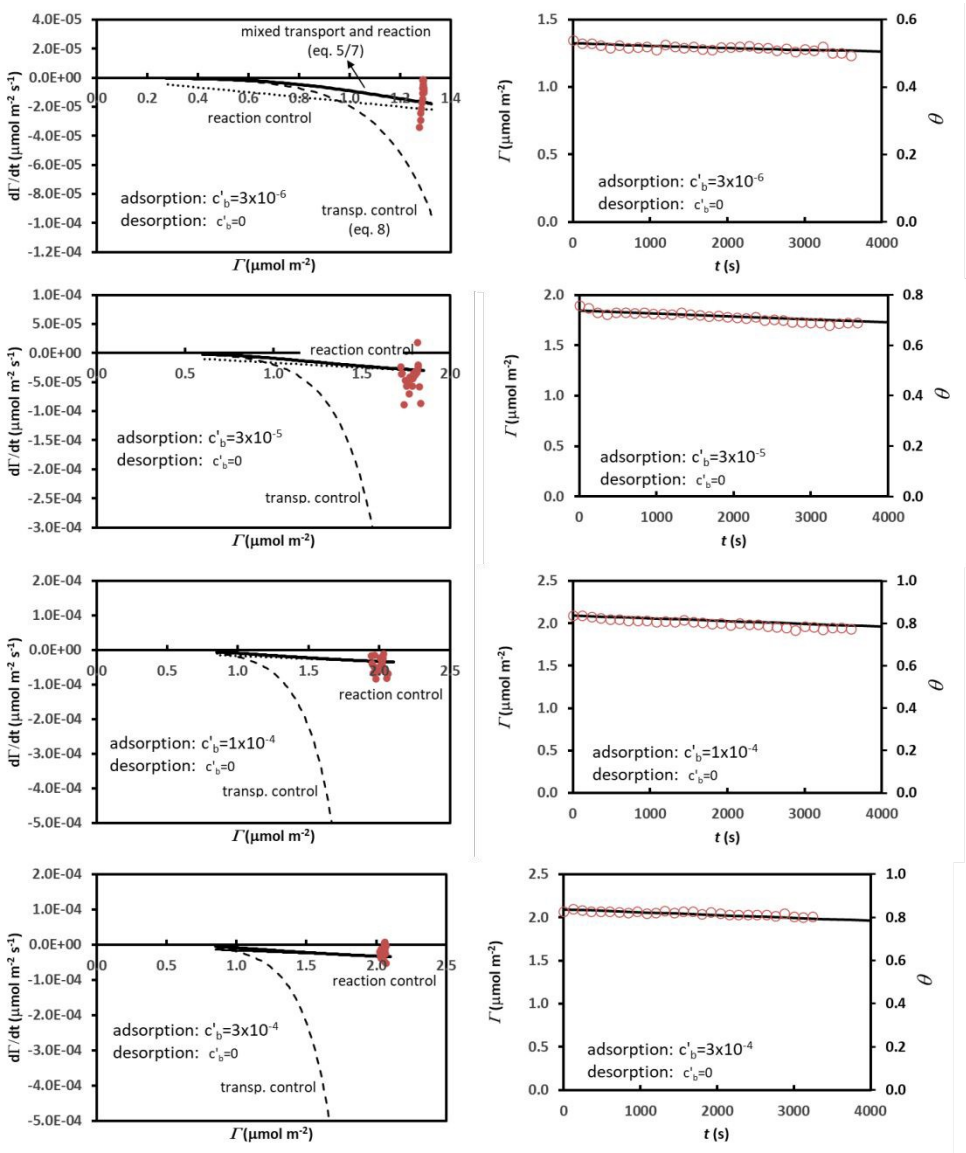

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Fig. 5. Desorption experiments. Rate vs Γ curves and desorption kinetic curves for the investigated cases. The concentration used for adsorbing phosphate are indicated in the figure. In all cases desorption took place by flowing supporting electrolyte at pH 7 (c'_b=0). Symbols correspond to experimental points and lines correspond to model calculations with parameters in Table 2. Γ vs. t curves were obtained by numerical integration (rectangle rule) of the general eq. 5.

The value of the first-order desorption rate constant, k_d=1.66×10^{-5} s^{-1}, indicates that the half-life of the desorption reaction ($t_{1/2}$=0.693/k_d) is 41700 s (11.6 h), and that almost 40 h should be necessary to desorb 90% of the adsorbed phosphate. On the contrary, adsorption would take only a few seconds in absence of transport control. This is why an almost full adsorption curve can be obtained in a short time, even under transport control, as seen in the right-hand side panels of Fig. 4, but only the initial parts of the desorption curves can be registered in one hour (right-hand side panels of Fig. 5).

Desorption kinetic studies are completely neglected in the literature. However, for the phosphate-goethite system studied here, detachment is slower than transport and controls the rate. Consequently, desorption kinetics shows to be more important than adsorption kinetics for determining rate coefficients from initial rates. This could be the case for many environmentally and technologically relevant systems. The explanation of the observed behaviour comes from the fact that in adsorption-desorption the transport process is always connected in series to the reaction process, and thus the overall rate is dictated by the slowest process. The case of phosphate on goethite is a typical example where the high affinity of the ion for the surface results in a large k_a and a small k_d. This combination of rate constants leads to a fast adsorption, which becomes transport-controlled, and a slow desorption, which becomes reaction-controlled. Many adsorbing substances in the environment or industry, having high affinity for the solid surface, with large k_a and small k_d, may behave as phosphate on goethite. With all these fast-adsorbing

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and slow-desorbing substances, measuring desorption kinetics is simpler and more informative than measuring adsorption kinetics.

It must be remarked that the measured adsorption and desorption rate constants are valid for the studied system at pH 7.0, which was the pH of the experiments. Changing pH changes the surface charge of the goethite surface and also may change the adsorbed species. For example, as indicated above, at pH 7.0 the phosphate species populating the goethite surface is a monoprotonated surface complex, whereas at low pH the prevailing species is a diprotonated surface complex (9). The rate constants at low pH are surely different because a different species is being adsorbed and desorbed. The methodology and model proposed here open the possibility of a realistic study of the very rich phosphate-goethite system, and many other systems where surface speciation changes by changing experimental conditions.

Conclusions

A simple, realistic and very effective model combining transport and reaction was successfully applied to describe simultaneously the adsorption-desorption kinetics at the solid/water interface as measured in an ATR-FTIR flow cell. The use of rate vs. adsorption curves ($\frac{d\Gamma}{dt}$ vs. Γ curves) is enlightening because it permits to compare actual rates with theoretical rates controlled either by transport or reaction, and to define if the process is being transport- or reaction-controlled.

The model was able to describe the behavior of the phosphate-goethite system under a variety of conditions, and the adsorption kinetic runs, the desorption kinetic runs and adsorption isotherms could be reproduced using just one set of rate coefficients. Since phosphate had a high affinity for the goethite surface the chemical attachment was very fast, making adsorption to be transport-controlled, and the chemical detachment was very

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slow, making desorption to be reaction-controlled. Therefore, obtaining reaction rate coefficients with this fast-adsorbing and slow-desorbing system was easier from desorption kinetic than from adsorption kinetic data.

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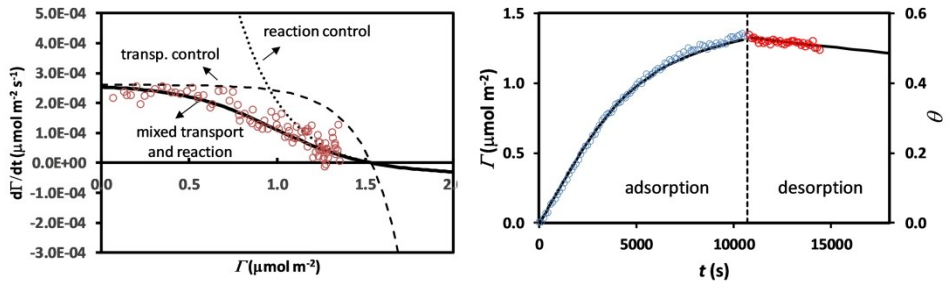

fast-adsorbing/slow desorbing systems: Easier to determine rate parameters from desorption kinetics

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