

Kinetics of Soil Chemical Reactions: Relationships between Empirical Equations and Diffusion Models

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ABSTRACT

A variety of kinetic equations such as zero-order, first-order, second-order, Elovich, fractional-power, and parabolic-diffusion equations have been used to describe the kinetics of soil chemical processes. Often, several of these expressions seem to equally well describe the kinetics of a particular reaction. In this research, it is shown that the kinetics of phosphate sorption/release can be described by an expression that is approximated at beginning times by a fractional-power equation, at intermediate times by the Elovich equation, and at long times by an apparent first-order equation. Such kinetics, which can be characterized by a sigmoidal $z(t)$ plot of the reciprocal of the rate against the time $[(dq/dt)^{-1}$ vs. $t]$, are consistent with theoretical homogeneous and heterogeneous models based on diffusion of the sorbate in the solid phase or at the solid/liquid interface. These models were applied to data from the published literature on sorption and release of phosphates by soils. For some soils, the experimental results were accounted for by assuming a constant diffusion coefficient. For other soils, it was assumed that diffusion processes with various diffusion coefficients take place simultaneously. Using these models, diffusion parameters can be estimated.

AN ARRAY of kinetic equations including zero-, first-, and second-order, Elovich, fractional-power, and parabolic-diffusion equations have been employed over the years to describe the kinetics of soil chemical phenomena (Sparks, 1989). In several cases, a number of these equations seem to equally well describe time-dependent data if simple correlation coefficients and standard errors of the estimate are the indices that are used to evaluate the data (Chien and Clayton, 1980; Onken and Matheson, 1982; Sparks and Jardine, 1984; Havlin et al., 1985).

The following expressions often describe time-dependent data well:

1. The fractional-power or modified Freundlich equation, which can be expressed as

$$q = kt^\nu \quad [1]$$

where q is the amount sorbed, k and ν are constants and ν is positive and smaller than one, and t is time. This expression is generally considered empirical, except for the case in which $\nu = 0.5$, where it becomes indistinguishable from the parabolic-diffusion equation.

Equation [1] and various modified forms of this equation have been applied to experimental data by several researchers (Cooke, 1966; Kuo and Lotse,

1974; Barrow and Shaw, 1975; Evans and Jurinak, 1976; Torrent, 1987; Elkhatib and Hern, 1988).

2. The Elovich equation,

$$q = A + (1/b) \ln(t + t_0) \quad [2]$$

where A, b and t_0 are constants. The Elovich equation is generally considered an empirical equation. In some cases, t_0 can be neglected and the equation reduces to a two-parameter equation. The Elovich equation has been used by several workers to describe soil chemical reaction rates (Chien and Clayton, 1980; Chien et al., 1980; Torrent, 1987).

3. The apparent first-order equation:

$$q/q_\infty = 1 - \alpha \exp(-\beta t) \quad [3]$$

where q_∞ is the amount sorbed at $t \rightarrow \infty$ and α and β are constants. Equation [3] is an integrated form of

$$dq/dt = \beta(q_\infty - q) \quad [4]$$

The apparent first-order equation is indistinguishable from a true first-order equation when q_∞ is independent of the concentration of the sorbate in solution and $\alpha = 1$. It has been used by numerous researchers to describe time-dependent data (Sparks, 1989, p.14-17).

There are many instances in the soil and environmental sciences literature where mechanistic meanings have been given to rate data solely on the fit of the data to one of these equations. However, deduction of reaction mechanisms based solely on the fit of the data to a particular equation has also been criticized (Sparks, 1987, 1989). Despite the wide applicability of one or more of these equations to various experimental results, there is no consistent relation between the equation that gives the best fit and the physicochemical and mineralogical properties of the soil-solute systems to which it is applied. Moreover, the kinetic equations that give the best fit are often empirical and the significance of the obtained rate parameters is unclear.

We have critically examined the inconsistencies and problems associated with the application of empirical equations to experimental rate data. The empirical equations that are widely applicable to soil chemical reactions are approximations to which more general expressions reduce in certain limited time ranges. These general expressions are characterized by S-shaped plots of $1/(dq/dt)$ vs. t and S-shaped plots of q vs. $\ln t$. They were formulated, tested, and shown to be consistently applicable to experimental results. (We use the terms S-shaped or sigmoid to characterize any $y(x)$ plot that has an inflection point, whether it is concave at small x and convex at large x , or whether it is convex at small x and concave at large x).

The S-shaped plots do not contradict the empirical equations whenever these are valid, and they can be explained by homogeneous and heterogeneous diffusion models. Additionally, some physically meaningful parameters, which can be used for predicting

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sorption phenomena in soils, can be calculated from the equations that characterize the S-shaped plots.

The treatment that follows is applied specifically to the data from the literature on sorption and release of phosphates by soils.

THEORETICAL DEVELOPMENT

A General Empirical Relation: S-Shaped $z(t)$ Plots

We have applied a kinetic relation, first suggested by Aharoni and Ungarish (1976), to the sorption and desorption of phosphates by soils. This relation stipulates that Elovichian kinetics are preceded and followed by non-Elovichian regimes.

Differentiating and rearranging Eq. [2] yields

$$z = (dq/dt)^{-1} = b(t + t_0) \quad [5]$$

Equation [5] implies that a plot of z vs. t consistent with Eq. [2] should be linear throughout the entire reaction period. However, the experimental plots of z against t are generally S-shaped: they are convex to the z axis at small t , concave at large t and have an inflection point at an intermediate t (Fig. 1). Elovichian kinetics are valid around the inflection point where the plot approaches linearity, the non-Elovichian kinetics apply before and after the Elovichian range.

It will be shown below that S-shaped $z(t)$ plots are consistent with Eq. [1] at small t and with Eq. [3] at large t . If Eq. [1] is differentiated and written as an explicit function of the reciprocal of the rate, the following is obtained:

$$z = (dq/dt)^{-1} = (1/\nu k)t^{1-\nu} \quad [6]$$

i.e., a plot of z against t that is convex to the z axis. Similarly, differentiating and reversing Eq. [3] obtains

$$z = (dq/dt)^{-1} = (1/q_\infty \alpha \beta) \exp(\beta t) \quad [7]$$

i.e., a plot of z against t that is concave to the z axis. The sigmoidal shape of the $z(t)$ plot means that the three empirical equations given above (Eq. [1], [2], and [3]) are applicable, each at a limited range of sorption.

There are indications that plots of z vs. t resulting in S-shaped relationships are valid even in the cases in which one of the simpler equations (Eq. [1], [2], or [3]) appears to be applicable throughout the entire reaction period that is measured. The rate of sorption often decreases with the amount sorbed by many orders of magnitude before saturation is approached. However, experimental methods are

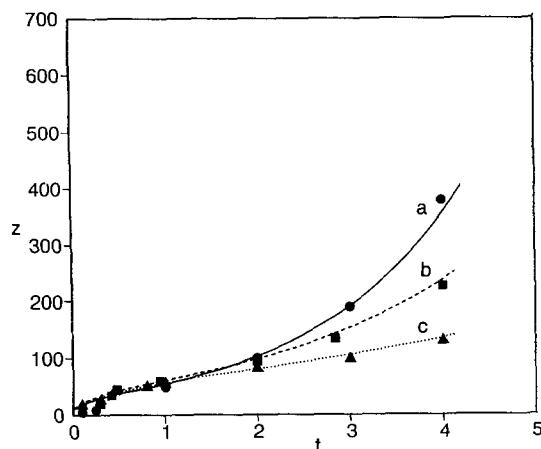


Fig. 1. Sorption of phosphate by three Greek soils (data of Polyzopoulos et al., 1986) as described by plots of $z((dq/dt)^{-1})$ in $\mu\text{g P g}^{-1} \text{h}^{-1}$ vs. t (in h), where q is the amount sorbed and t is time: (a) Typic Haploxeralf, (b) Ultic Paleixeralf, (c) Typic Dystrachrept.

usually designed for the measurements of rates varying within a shorter range, e.g., two to three orders of magnitude. There are cases, therefore, in which the measured data points represent only a limited part of the complete process. In these cases, the rate may seem to become zero before true equilibrium is approached, or the measured process may appear to be preceded by an instantaneous one. One of the simple

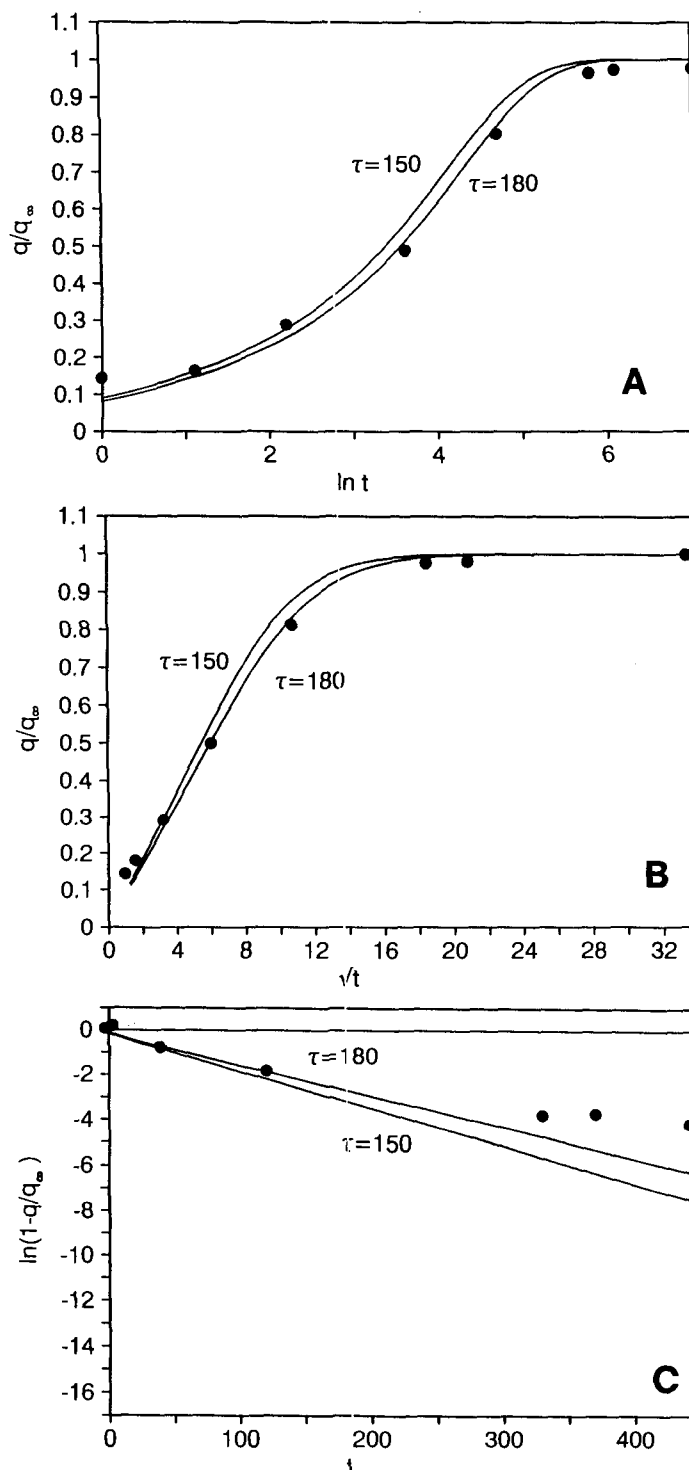


Fig. 2. Sorption of phosphate by the $<2\text{-mm}$ fraction of a soil (data of Enfield, 1974). Curves were calculated according to Eq. [8] with $\tau = 150$ and 180 h: (a) plot of q/q_∞ vs. $\ln t$, (b) plot of q/q_∞ vs. $t^{1/2}$, (c) plot of $\ln(1 - q/q_\infty)$ vs. t , where q is the amount sorbed and q_∞ is the amount sorbed at time $t \rightarrow \infty$.

equations (Eq. [1], [2], or [3]) would be applicable during the entire experimental time if all the measured points are at times during which the assumptions underlying the equation are valid.

It also should be noted that the fractional-power equation (Eq. [1]) or the Elovich equation (Eq. [2]) cannot be valid when t is large, as they give $q \rightarrow \infty$ when $t \rightarrow \infty$. At some time, an equation that predicts a finite saturation value of q at $t \rightarrow \infty$, such as the apparent first-order equation (Eq. [3]), must be applicable. On the other hand, the constant α that has to be fitted if Eq. [3] is used is generally > 1 , indicating that the apparent first-order equation is not valid when t is sufficiently small. Therefore, we assume that, although the kinetics of phosphate sorption by soils appear to be described by various empirical expressions, the expression that describes the kinetics of the overall process is characterized by a plot of z against t that is S-shaped.

Because kinetic data are often measured as amounts sorbed at various times and reported as plots of q vs. $\ln t$, it is useful to examine what form these plots should have if the above relationship is obeyed. It can be shown easily that plots of q vs. $\ln t$ should also be S-shaped, but with opposite curvature. In the region corresponding to the fractional-power equation (Eq. [1]), the slope $dq/d \ln t$ increases [$dq/d \ln t = \nu k \exp(\nu \ln t)$]. At the region corresponding to the Elovich equation (Eq. [2]), the slope is constant [$dq/d \ln t = 1/b$, neglecting t_0], while the region corresponding to the apparent

first-order equation (Eq. [3]) has a decreasing slope [$dq/d \ln t = q_\infty \alpha \beta t \exp[-\beta \exp(\ln t)]$].

The plot of q/q_∞ vs. $\ln t$ for the sorption of phosphate by a gravelly sandy loam (Enfield, 1974), reproduced in Fig. 2a, is S-shaped as expected. It is approximately linear between $t \approx 10$ h and $t \approx 100$ h (range of validity of the Elovich equation). When the data are replotted as q vs. \sqrt{t} (Fig. 2b) the plot obtained is linear for $t < 50$ h (range of validity of the fractional-power equation). The data of Ryden (1977) for the sorption of phosphate on soil refer to the range at which the Elovich equation is applicable, as pointed out by Chien and Clayton (1980) (Fig. 3). However, a decrease of slope at large t consistent with the one observed in Fig. 2a is discernible.

Theoretical Diffusion Models

Appropriate kinetic models should lead to equations consistent with the above rule, i.e., a plot of z vs. t that is S-shaped with minimum slope at the inflection point or, alternatively, a plot of q vs. $\ln t$ that is S-shaped with a maximum slope at the inflection point. Models based on diffusion satisfy these conditions (Aharoni and Suzin, 1982a,b; Aharoni, 1984), and it will be shown below that the experimental results can be fitted by models based on diffusion in either a homogeneous medium or a heterogeneous medium. A more complex mathematical development of these models is given in the Appendix.

Models Based on Diffusion in a Homogeneous Medium

In these models, it is assumed that a soil constituent is mainly responsible for the sorption of the solute and that the rate-controlling process is diffusion of the sorbed solute in that soil constituent. It is further assumed that particle size and the diffusion coefficient do not vary considerably. If the flux of the sorbate is essentially a parallel flux, integration of Fick's equation gives

$$q/q_\infty = 1 - \sum_{n=0}^{\infty} (2/b_n) \exp(-b_n t/\tau) \quad [8]$$

Here, τ is defined by $\tau = r^2/D$, where r is the length of the diffusion path and D is the diffusion coefficient; b_n is defined by $b_n = \pi^2(2n + 1)^2/4$, where n is an integer.

A plot of the dimensionless variable $z_r = [d(q/q_\infty)/d(t/\tau)]^{-1}$ vs. the dimensionless time t/τ corresponding to Eq. [8] is depicted in Fig. 4. It is S-shaped with a minimum slope at the inflection point, in agreement with the S-shaped $z(t)$ rule. A plot of q/q_∞ vs. $\ln(t/\tau)$ corresponding to Eq. [8] is depicted in Fig. 5a. It is also consistent with the above rule, i.e., it is S-shaped with a maximum slope at the inflection point.

Applicability of Eq. [8] does not imply a specific type of diffusion. This equation may reflect occlusion in a network of micropores, penetration into the bulk of the solid, surface diffusion, or other diffusion processes. It implies, nevertheless, that the diffusivity and the length of the diffusion path are the same everywhere in the reacting system, that the flux is a parallel one, and that the concentration of the sorbate at the boundary of the diffusion medium is constant.

Equation [8] is one of the solutions of the diffusion equation that leads to an S-shaped plot of z vs. t and consequently to applicability of the fractional-power equation, the Elovich equation, and the apparent first-order equation at consecutive ranges of t . Various other solutions of the diffusion equation have that property, and this explains why the S-shaped $z(t)$ plot has wide applicability. A simple procedure for finding out if a given solution of the diffusion equation leads to an S-shaped $z(t)$ plot is given in the Appendix.

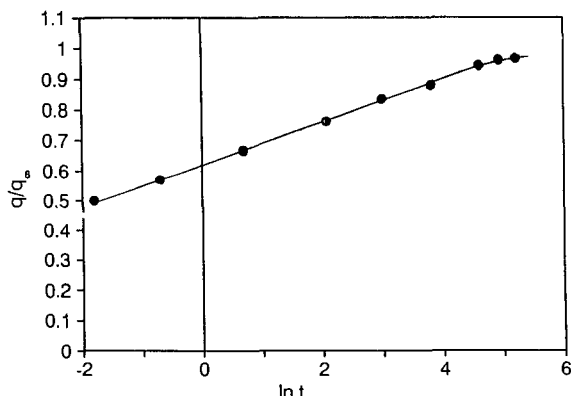


Fig. 3. Sorption of phosphate by a soil (data of Ryden et al., 1977) as described by a plot of q/q_∞ against $\ln t$ (t in h), where q is the amount of phosphate sorbed and q_∞ is the amount sorbed at time $t \rightarrow \infty$.

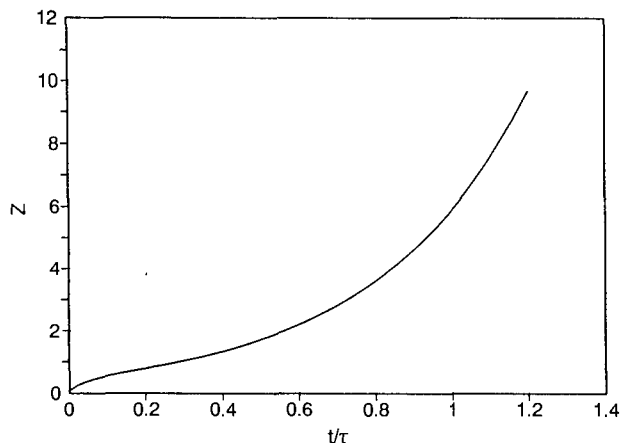


Fig. 4. Plot of z_r against t/τ , according to Eq. [8], where $z_r = [d(q/q_\infty)/d(t/\tau)]^{-1}$, q is the amount of phosphate sorbed, q_∞ is the amount sorbed at time $t \rightarrow \infty$, and $\tau = r^2/D$, where r is the length of the diffusion path and D is the diffusion coefficient.

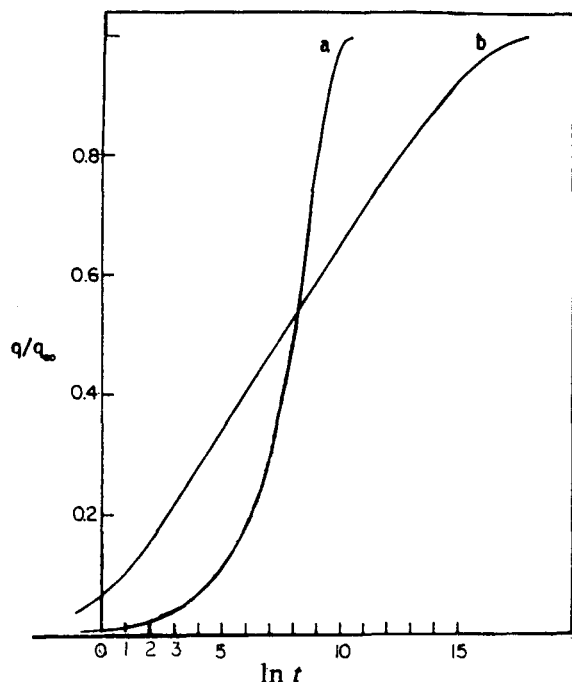


Fig. 5. Theoretical plots of the amount of phosphate sorbed (q) vs. $\ln t$, where t is time: Curve (a) plot of q/q_∞ vs. $\ln t$ calculated according to Eq. [8] for $\tau = 5800$ time units, where q_∞ is the amount sorbed at $t \rightarrow \infty$; Curve (b) plots of q/q_∞ vs. $\ln t$ calculated according to Eq. [13] for the distribution $q_{\tau\infty}(\tau) = C/\tau$ (where q_∞ is the sorption of solute at equilibrium and C is a constant), with the smallest τ (τ_i) = 1.95 and the largest τ (τ_m) = 173×10^7 .

Diffusion in a Heterogeneous Medium

In this model, it is assumed that diffusion processes with various diffusion coefficients and various particle sizes take place simultaneously, and the observed sorption of solute is determined by the sum of these processes. The simplifying assumption that each component process can be assigned a constant value of τ is introduced. The overall solute uptake q at time t is given by

$$q = \int_{\tau_i}^{\tau_m} q_{\tau\infty}(q_{\tau t}/q_{\tau\infty}) d\tau \quad [9]$$

where $q_{\tau t}$ and $q_{\tau\infty}$ are the sorption of solute at t and at equilibrium, respectively, and τ_i and τ_m are the smallest and largest τ , respectively, in the system. An expression for the time dependence of q is obtained by introducing a relation between $q_{\tau t}/q_{\tau\infty}$ and t as the one given in Eq. [8] and using an appropriate distribution $q_{\tau\infty}(\tau)$.

Equation [9] can be solved analytically for the specific distribution

$$q_{\tau\infty}(\tau) = C/\tau \quad [10]$$

where C is a constant (Aharoni and Suzin, 1982b) and employing the fact that Eq. [8] can be approximated at small t and large t by simple expressions. The expression obtained is

$$\frac{d(q/q_\infty)}{d \ln t} = \frac{1}{\rho} \left[1 - \left(\frac{4t}{\pi\tau_m} \right)^{1/2} - \frac{8}{\pi^2} \exp\left(-\frac{\pi^2 t}{4\tau_i}\right) \right] \quad [11]$$

where

$$\rho = \ln(\tau_m/\tau_i) \quad [12]$$

For τ_i small and τ_m large, there is an appreciable range of t at which the two negative terms in Eq. [11] are negligible and it then reduces to

$$d(q/q_\infty)/d \ln t = 1/\rho \quad [13]$$

At small t , the third term on the right-hand side of Eq. [11] is not negligible, and, at large t , the second term is not negligible, i.e., the slope $d(q/q_\infty)/d \ln t$ is smaller than $1/\rho$ at small t and at large t . This indicates that a plot of q/q_∞ against $\ln t$ has the required S-shape (see Fig. 5b). It can be shown that the slope of the curve is not significantly affected by the distribution $q_{\tau\infty}(\tau)$ used in the calculation.

The plot of z vs. t corresponding to Eq. [11] is

$$z = \frac{\rho t}{q_\infty} \left[1 - \left(\frac{4t}{\pi\tau_m} \right)^{1/2} - \frac{8}{\pi^2} \exp\left(-\frac{\pi^2 t}{4\tau_i}\right) \right]^{-1} \quad [14]$$

and it also has the required S-shape.

Comparison of Diffusion Models

In homogeneous and heterogeneous models, plots of the relative sorption (q/q_∞) vs. $\ln t$ are S-shaped in both cases (see Fig. 5). However, they differ in the following two respects:

1. For diffusion in a homogeneous medium, the range of validity of Eq. [2] is narrow compared with the range of validity of Eq. [1] and [3]. For heterogeneous diffusion, the range of validity of Eq. [2] corresponds to the range over which the two negative terms in Eq. [11] can be neglected; this range is wide if τ_i is small and τ_m is large, i.e., it increases with the heterogeneity of the system.
2. The slope $d(q/q_\infty)/d \ln t$ at the linear part (range of validity of Eq. [2]) is given for heterogeneous diffusion by $1/\rho$ (Eq. [13]), i.e., the slope decreases when the heterogeneity represented by the ratio τ_m/τ_i increases. The maximum possible slope is the one for a homogeneous system, which was estimated from Eq. [8] and found to be about 0.24 (Aharoni and Suzin, 1982a). It is noted that this value does not depend on τ , as $d(q/q_\infty)/d \ln t = d(q/q_\infty)/d \ln(t/\tau)$. It is also noted that Eq. [13] is valid only if τ_m and τ_i vary widely, otherwise the slope approaches the maximum value 0.24.

It is also possible to discriminate between the two diffusion models by considering plots of zq_∞ vs. t . For heterogeneous diffusion, the linear part of the plot corresponding to Eq. [2] is more pronounced and is characterized by a steeper slope than what is observed for homogeneous diffusion.

APPLICATIONS TO EXPERIMENTAL DATA

A plot of q/q_∞ vs. $\ln t$ for phosphate sorption by a Chigley gravelly sandy loam, depicted in Fig. 2a, (Enfield, 1974) has a shape similar to the one in Fig. 5a, and the slope at the linear part around the inflection point is about 0.24. These properties are consistent with Eq. [8]; however, plots calculated with various τ indicate that the homogeneous model, while more correct than the heterogeneous model, is only approximately valid. The data can be fitted with τ between 150 and 180 h, but the best value of τ increases slightly with t . Figure 2c shows that phosphate sorption continues at conditions at which the rate of sorption according to $\tau = 180$ h should approach 0. The contribution of the diffusion processes with higher τ become dominant at this range of t .

Plots of q vs. $\ln t$ that obey one of the equations given above, i.e., the fractional-power (Eq. [1]), the Elovich (Eq. [2]), or the apparent first order (Eq. [3]) during

the entire reaction-rate period represent an incomplete isotherm and are more difficult to interpret. However, it is reasonable to assume that a plot that obeys the Elovich equation during the entire experiment, with a slope $d(q/q_\infty)/d \ln t$ that is significantly smaller than 0.24 should reflect sorption in a heterogeneous medium. If diffusion processes with widely different diffusion coefficients take place simultaneously, the variation in the observed rate is important and the rate can become very small before true equilibrium is achieved. Equation [13] would seem to be valid indefinitely.

For data obeying the Elovich equation with $d(q/q_\infty)/d \ln t < 0.24$, it is possible to evaluate the ratio τ_m/τ_i by applying Eq. [13], provided that saturation is finally approached and q_∞ is known. Otherwise, only a minimum value for the ratio τ_m/τ_i can be estimated. The data of Ryden et al. (1977) for the sorption of phosphate on soil (Fig. 3) are consistent with diffusion in a heterogeneous medium and it seems that saturation was approached during the run. The slope $d(q/q_\infty)/d \ln t$ is ≈ 0.07 . The corresponding ratio τ_m/τ_i is of the order of 10^7 , indicating a very large span of diffusion coefficients. The data of Amer et al. (1955) for the release of phosphates from a soil clay (Fig. 6) also indicate diffusion in a heterogeneous medium. Complete depletion is not approached, and q/q_{maximum} can be evaluated but not q/q_∞ . The slope $d(q/q_\infty)/d \ln t$ is < 0.13 and the corresponding estimation of the ratio between largest and smallest τ is $\tau_m/\tau_i > 10^3$.

DISCUSSION

It is generally believed that, when the rate of sorption is rapid, the rate-limiting step is probably a transport process taking place in the liquid phase, such as diffusion in the bulk of the liquid, at the film adjacent to the solid particle, in liquid-filled pores, etc. When the rate of sorption is slow, it is likely that processes taking place at the solid phase are rate determining (Aharoni and Sparks, 1991). However, the nature of the processes taking place at the solid phase are not well understood. Our investigation, which used published studies on phosphate sorption and release kinetics from soils, suggests that the rates are diffusion controlled. Empirical equations such as the fractional-power function, Elovich, and apparent first-order, which have wide applicability to rate processes in soils, indicate the validity of S-shaped $z(t)$ and $q(\ln t)$ plots. The simplest explanation for this type of relationship is diffusional kinetics.

The fact that diffusional kinetics are obeyed does not mean that sorption does not include slow chemical reactions. Rather, such a finding indicates that the kinetics of chemical processes cannot be considered separately from transport phenomena. Thus, such a combination of processes cannot be treated using first-order or other-order chemical kinetics equations. When one states that a reaction between the molecular species A and B is of first order with respect to A , one assumes that the molecules of A have equal chances of participating in the reaction and therefore the rate is proportional to the concentration C_A . This reasoning can be extended to a reaction between an adsorbing surface and an adsorptive solute. The concentration

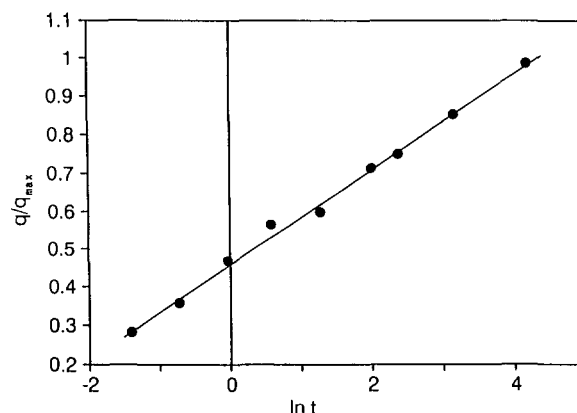


Fig. 6. Release of phosphate by a soil clay (data of Amer et al., 1955) as described by a plot of q/q_{maximum} vs. $\ln t$ (t in h), where q is the amount of phosphate sorbed, q_{maximum} is the maximum amount sorbed, and t is time.

C_A , in this case, refers to the number of reactive sites per unit area, which corresponds to the number of unoccupied sites per unit area ($1 - \theta_A$). However, by using first-order kinetics (or other-order kinetics) one tacitly assumes that all of the surface sites are potential reactants at any time, and they have an opportunity of participating in the sorption process. If one assumes that there are sites that cannot be reached directly from the fluid phase, but can be reached after the sorbate has undergone sorption and desorption at other sites, one cannot separate chemical kinetics from transport kinetics. The overall kinetic process obeys a diffusion equation. However, the diffusion coefficient, which reflects the rate at which the sorbate jumps from one site to another, is determined by the rate of the chemical reactions by which the sorbent-sorbate bonds are created and destroyed. Additionally, the activation energy for diffusion is equivalent to the activation energy of the chemical reaction.

The conclusion that S-shaped $z(t)$ plots and diffusional kinetics have wide applicability independent of the nature of the soil and of the experimental conditions does not imply that variables such as soil texture, mineralogical composition, nature of the sorbate, ionic strength, pH, etc., are of secondary importance in affecting sorption reactions. Widely different kinetic expressions may have in common the fact that they reflect some solution of the diffusion equation. One can state that kinetics of anion sorption on soils have some common characteristics. However, the actual kinetic expressions have to be defined for each case and it should be possible to correlate them to the sorption conditions.

It is unlikely that analyses of kinetic data would give precise information concerning the diffusion processes that are rate determining. Various possible processes give results that are indistinguishable from one another. However, analyses of the kinetic data can indicate if homogeneous or heterogeneous diffusion models are valid and can allow an estimation of the magnitude of τ , which represents the ratio r^2/D . This information, although incomplete, can be valuable in understanding the mechanism of sorption and in predicting the behavior of large-scale soil systems.

APPENDIX

Diffusion Equations Corresponding to S-Shaped z(t) Plots

The equation for diffusion in slabs (Eq. [8]) can be approximated at small t by (Aharoni and Suzin, 1982a)

$$q/q_{\infty} = k_s (t/\tau)^{1/2} \quad [A1]$$

where $k_s = 1.128$ and the corresponding $z(t)$ plot is

$$z = (2\tau^{1/2}/k_s q_{\infty}) t^{1/2}. \quad [A2]$$

At large t , it is approximated by

$$q/q_{\infty} = 1 - k_r \exp(-\alpha t/\tau) \quad [A3]$$

where $k_r = 0.811$ and $\alpha = 2.467$. The corresponding $z(t)$ plot is

$$z = (\tau/k_r \alpha q_{\infty}) \exp(\alpha t/\tau). \quad [A4]$$

As Eq. [A2] indicates, a plot of z vs. t is convex towards the z axis and Eq. [A4] yields a concave plot. The plot of z vs. t for the overall equation has to be S-shaped, as shown when z vs. t is calculated using Eq. [8] (Fig. 4).

Examination of the small- t and large- t approximations corresponding to solutions of the diffusion equations indicates whether these solutions are consistent with S-shaped $z(t)$ plots. It can be shown that many solutions are, in fact, consistent with S-shaped $z(t)$ plots. It is easy to show that this applies to diffusion into spheres and cylinders. For spheres, Eq. [A1] to [A4] apply with $k_s = 3.385$, $k_r = 0.607$, and $\alpha = 9.869$. For cylinders, Eq. [A1] to [A4] apply with $k_s = 2.256$, $k_r = 0.692$ and $\alpha = 5.783$.

Derivation of Equations [11] and [14]

Considering Eq. [9], one assumes that the fractional uptake q_t/q_{∞} at a patch characterized by τ is given by Eq. [8]. One further assumes that Eq. [8] can be approximated by Eq. [A1] from $t/\tau = 0$ up to $t/\tau = 0.192$ and by Eq. [A3] from $t/\tau = 0.192$ up to $t/\tau = \infty$ (the plot of z vs. t/τ has an inflection point at $t/\tau = 0.192$).

Instead of considering a process with a given τ at various t , let us consider the situation at a given t in an array of processes with various τ . One can then assume that the processes with $\tau > \tau_i = t/0.192$, which have not yet reached the inflection point, are still sorbing according to Eq. [1], whereas the processes with $\tau < \tau_i = t/0.192$ are already sorbing according to Eq. [A3]. One can, therefore, rewrite Eq. [9] as

$$q = \int_{\tau_i}^{\tau_m} q_{\infty} k_s (t/\tau)^{1/2} d\tau + \int_{\tau_i}^{\tau_m} q_{\infty} [1 - k_r \exp(-\alpha t/\tau)] d\tau \quad [A5]$$

Introducing the distribution $q_{\infty}(\tau) = C/\tau$ and noting that

$$q_{\infty} = \int_{\tau_i}^{\tau_m} q_{\infty} d\tau = C\rho, \quad [A6]$$

one obtains

$$\rho q/q_{\infty} = \int_{\tau_i}^{\tau_m} (1/\tau) k_s (t/\tau)^{1/2} d\tau + \int_{\tau_i}^{\tau_m} (1/\tau) [1 - k_r \exp(-\alpha t/\tau)] d\tau. \quad [A7]$$

Differentiating according to t and multiplying both sides by t gives Eq. [11]. Equation [14] is derived from Eq. [11], noting that $d(q/q_{\infty})/d \ln t = t/q_{\infty} z$.

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