

Analyses of Adsorption Kinetics Using a Stirred-Flow Chamber:

I. Theory and Critical Tests

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ABSTRACT

The study of ion-exchange kinetics on soils and soil constituents has attracted much interest throughout the last decade. The introduction of a stirred-flow method to study these reactions, as well as other adsorption-desorption phenomena, has stimulated this interest. However, the manner in which rate data are interpreted using this technique and other flow methods has been questioned. Accordingly, a numerical solution for various instantaneous equilibrium and kinetic models is presented. It was found that rate data that could be described using an instantaneous equilibrium model could also be interpreted using a kinetic model. Therefore, the validity of kinetic rate coefficients obtained by flow methods is questionable. An analytical approach was developed to outline experimental methods that could be used to distinguish between instantaneous equilibrium and time-dependent reactions and to differentiate between solution-concentration-dependent kinetic models vs. those that are independent of solution concentration. By using this approach, and employing various flow rates and influent concentrations, as well as using a stopped-flow technique, it is easy to decide whether rates of reactions can be measured using the stirred-flow method for specific experimental conditions.

HISTORICALLY, the study of ion-exchange kinetics on soils has received less attention than chemical-equilibrium studies. During the last decade, however, much interest has been generated concerning ion-exchange kinetics. However, the problems of correctly interpreting the experimental results and making comparisons between different kinetic methods have not been solved (Sparks, 1989). For example, in comparing the magnitude of rate coefficients for K-Ca exchange on two clay minerals and a soil, Ogwada and Sparks (1986) found that the rate coefficients were greatly affected by the type of kinetic method.

To enable measurements of rapid reactions and to minimize transport phenomena, a new method, re-

ferred to as a stirred-flow technique, was developed by Carski and Sparks (1985). This method combines some of the favorable aspects of both batch and miscible-displacement techniques. However, the data analyses employed by Carski and Sparks (1985) were based solely on the calculated adsorbed quantities, which are not measured directly. Consequently, this could lead to experimental and mathematical errors, and data analyses should be based on effluent solution concentration (Schnabel and Fitting, 1989).

Fundamentally, all chemical reactions are time dependent but, if the reaction is too rapid to be determined by the employed method or under the specific conditions used in the measurements, the process can be defined as an instantaneous one. The flow methods used in soil chemistry for determination of kinetic rate coefficients are based on measurements of solution-concentration change vs. time (Sparks, 1986, 1989). Consequently, the adsorbed amount as a function of time is also a function of solution concentration. These techniques have been used for studying adsorption isotherms, assuming instantaneous equilibrium (Egozy, 1980; Isaacson and Hayes, 1984; Miller et al., 1989).

In a previous study (Seyfried et al., 1989), we posed the possibility that the cation-exchange reaction on soils is very rapid and, if the stirred-flow method is used under experimental conditions such as those described by Carski and Sparks (1985), a kinetic process is not measured. Rather, what occurs is a process of solution dilution in the chamber combined with an instantaneous equilibrium exchange reaction.

Therefore, there is a need to establish systematic tests to distinguish between instantaneous and time-dependent reactions for a range of experimental conditions, and between different types of kinetic models. The objectives of this paper are to develop experimental techniques to distinguish between: (i) instantaneous and time-dependent reactions; and (ii) kinetic reactions that are dependent on solution concentration vs. those that are independent using the stirred-flow chamber.

MATERIALS AND METHODS

Theoretical Considerations

Stirred-Flow System

The following analyses of flow through the stirred-flow chamber are similar to those presented by Skopp and

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McCallister (1986). Their theoretical development was based on a miscible-displacement technique similar to that used by Sparks et al. (1980), and not on the stirred-flow method. However, their assumption of no concentration gradient between inlet and outlet ports, which is also used in our analyses below, is better applied to the stirred-flow method, as was shown by Seyfried et al. (1989). In the equations that are developed below, we shall use the notation of Seyfried et al. (1989). The analyses are based on the following equations for mass balance (Eq. [1] and [1a] for a chamber without and with adsorbent, respectively):

$$\begin{aligned} C_i J &= J C_{\text{out}} + V_c dC/dt & [1] \\ C_i J &= J C_{\text{out}} + V_c dC/dt + M dS/dt & [1a] \end{aligned}$$

where

C_i = influent concentration, mol m⁻³
 C_{out} = effluent concentration, mol m⁻³
 C = chamber solution concentration, mol m⁻³
 J = flow rate, m³ min⁻¹
 t = time, min
 V_c = solution volume in the chamber, L
 S = amount adsorbed, mol kg⁻¹
 M = adsorbent mass, kg

The mass-balance equation expressed in Eq. [1a] was first presented, in a similar form, by Denbigh (1944) for kinetic studies using a stirred-flow reactor. Equation [1] can be solved analytically for the initial condition, $t = 0$ and $C = 0$, assuming a well-mixed system, which implies that $C = C_{\text{out}}$ (Denbigh, 1944). The solution is

$$C = C_i [1 - \exp(-Jt/V_c)] \quad [2]$$

The well-mixed assumption was evaluated and found to be valid for experimental conditions where the reaction-chamber volume was 8.3 cm³ and flow rate ranged from 0.28 to 2.20 mL min⁻¹ (Seyfried et al., 1989). Therefore, in the subsequent equations, C_{out} will be substituted by C .

Skopp and McCallister (1986) presented an analytical solution for Eq. [1a] using the following four rate laws:

$$dS/dt = -k_{-1}S + k_1C(E - S) \quad [3a]$$

$$dS/dt = -k_{-1}S + k_1(E - S) \quad [3b]$$

$$dS/dt = -k_{-1}S^n + k_1C^m \quad [3c]$$

$$dS/dt = -k_{-1}S + k_1C/(k_2 - C) \quad [3d]$$

where

k_{-1} = reverse rate coefficient
 k_1 = forward rate coefficient
 k_2 = empirical rate coefficient
 E = adsorption maximum, mol kg⁻¹
 n and m = adsorption coefficients (dimensionless)

The units of the rate coefficients depend on the particular equation that is used, i.e., min⁻¹ for k_1 and L mol⁻¹ min⁻¹ for k_{-1} in Eq. [3a], and min⁻¹ for k_1 and k_{-1} in Eq. [3b]. Equation [3a] is a kinetic model based on the Langmuir equation, Eq. [3b] is a first-order equation, and Eq. [3c] and [3d] are empirical fractional-order equations.

Equation [1a] in combination with Eq. [3a] to [3d] were solved by Skopp and McCallister (1986) only for limited cases. Fortunately, numerical solutions for systems containing nonlinear ordinary differential equations are available. We used the procedure DO2BBF of the NAG library (Numerical Algorithms Group, 1984) in this study, but other procedures can be used as well. Using this procedure, Eq. [1a] is rearranged as

$$dC/dt = (J/V_c)(C_i - C) - (M/V_c)(dS/dt) \quad [4]$$

Substituting dS/dt into the right side of Eq. 3a to 3d, ordinary differential equations are formed. Using Eq. [3a], the following equation is obtained:

$$dC/dt = (J/V_c)(C_i - C) - (M/V_c)[-k_{-1}S + k_1C(E - S)] \quad [5]$$

Equations [5] and [3a] are introduced into the algorithm for prediction of C and S as a function of time for known rate coefficients. This method can be used to solve Eq. [1a] using rate laws given in Eq. [3a] to [3d] and numerous other rate laws.

Equation [1a] was solved for an initial condition defined by $C = 0$, $S = 0$, $t = 0$. This initial condition conforms to an adsorption process starting with zero concentration of the adsorbed cation in the chamber solution and on the solid phase. The desorption process can be simulated using $C_i = 0$ and the initial condition $C = C_o$, $S = S_o$, $t = 0$, where C_o and S_o are the initial solution concentration and adsorbed quantity of the studied cation, respectively. Although not shown, the numerical solutions of Eq. [1a] in combination with Eq. [3a] to [3d] were evaluated by comparing the results with the analytical solutions presented by Skopp and McCallister (1986).

We followed the method of Seyfried et al. (1989) in establishing what magnitude of reaction rates could be distinguished from instantaneous equilibrium for an adsorption process that is dependent on solution concentration. Considering a linear or nonpreference isotherm such as that at equilibrium,

$$S/E = (C/C_T) \quad [6]$$

where C_T is the sum of competing ions (mol m⁻³), Seyfried et al. (1989) suggested the following empirical kinetic model, in which adsorption is dependent on solution concentration as well as time:

$$S/E = (C/C_T)[1 - \exp(-kt)] \quad [6a]$$

where k is an apparent forward rate coefficient (min⁻¹).

There are two reasons that Eq. [6a] was used. First, it has the property that very slow reactions (small k values) approximate the nonadsorbed condition while very rapid reactions (large k values) approximate the instantaneous-adsorption case given in Eq. [6]. Second, reaction rates can be described in terms of a reaction half-time ($t_{1/2}$) that is analogous to the half-life used to describe radioactive decay. Values of k can be calculated from $t_{1/2}$ values using the relationship

$$k = (-\ln 0.5)/t_{1/2} \quad [7]$$

To solve Eq. [1a] using Eq. [6] or [6a], the latter equations must be derived with respect to time (assuming that C changes with time, a necessary condition for the stirred-flow chamber method):

$$dS/dt = E(1/C_T)dC/dt \quad [8]$$

$$dS/dt = E\{(C/C_T)k \exp(-kt) + (1/C_T)[1 - \exp(-kt)]dC/dt\} \quad [9]$$

Equation [9] can be simplified such that:

$$dS/dt = (S/C)dC/dt + k[E(C/C_T) - S] \quad [10]$$

One of the most successful models for describing the kinetics of ion adsorption on soils and clays has been a first-order equation (Eq. [3b]) or a version of this equation, in which just the forward reaction is considered (Carski and Sparks, 1985; Hodges and Johnson, 1987; Jardine and Sparks, 1984; Ogwada and Sparks, 1986; Sparks et al., 1980):

$$dS/dt = k_1(E - S) \quad [11]$$

In both versions (Eq. [3b] and [11]), adsorption is independent of solution concentration; therefore, Eq. [11] can be integrated independently of Eq. [1a]. For the initial condition, at $t = 0$, $S = 0$, the analytical integration is

$$\ln(1 - S/E) = -k_1 t \quad [12]$$

Stopped-Flow System

An additional mass-balance equation was used for the stopped-flow test, replacing Eq. [1a]:

$$CV_c + SM = S_c \quad [13]$$

where S_c = total quantity of adsorbate ion S in the chamber, in mol. Equation [13] in combination with Eq. [3b], [6], or [6a] can be solved analytically or numerically (DO2BBF of NAG) for calculation of the adsorbed fraction and the solution concentration as a function of stopping time. The solution-concentration and adsorbed-fraction values obtained from Eq. [13] were introduced as initial conditions for solving Eq. [1a] in combination with the respective model describing the remaining continuous run after the flow was restarted.

RESULTS AND DISCUSSION

Graphs of $\ln(1 - S/E)$ vs. t are commonly used to test the validity of a first-order equation (Sparks, 1986). In estimating kinetic rate coefficients using flow method, however, one has to test carefully that kinetic phenomena are being measured rather than instantaneous-equilibrium processes. For example, a non-preference exchange reaction between two homovalent cations in ideal solutions obeys Eq. [6]. This equation can fit some cases of heterovalent cation exchange that depend on ionic strength without assuming nonpreference. Equation [6] in combination with Eq. [1a] can be integrated analytically such that

$$\ln(1 - S/E) = -[JC_c/(ME + C_T V_c)]t \quad [14]$$

Thus, plots of $\ln(1 - S/E)$ vs. t for an instantaneous-equilibrium process described by Eq. [6] are linear but their slopes do not have any kinetic meaning, not even as apparent rate coefficients. In such cases, predictions of adsorption as a function of time using the known parameters J , C_i , M , E , and V_c are more convenient, and have a better scientific basis than determining a rate coefficient for each set of experimental conditions. Consequently, it is questionable to fit kinetic models to adsorption data obtained using a flow method, without other experimental tests to validate the kinetic model.

The above discussion and the results of Seyfried et al. (1989) indicate the need for criteria to measure kinetic parameters using the stirred-flow chamber and similar flow methods. Such criteria were presented by Seyfried et al. (1989) assuming, a priori, an equilibrium model (Eq. [6]) and a kinetic model (Eq. [6a]). But in reality, when the kinetic model is not known, there is a need to develop a general method to distinguish between instantaneous equilibrium and kinetic models that are solution-concentration dependent and solution-concentration independent before fitting models and determining apparent rate coefficients. Experimental tests are suggested below for determining cation-adsorption rate coefficients for a specific range of experimental conditions using flow methods, and for choosing kinetic models that are dependent on or independent of concentration. This study does not deal with the statistical examination of models, which is an important step in comparing models. The goal of the suggested experimental tests is to provide means for rejecting improper models before conducting sta-

tistical tests. The aim is to present hypotheses and, by analyzing them, to suggest experimental tests that clearly distinguish between the models (Chamberlin, 1890; Platt, 1964). This approach is especially justified when one wishes to measure a parameter and wants to be sure that this parameter is independent of other factors.

The proposed tests are: (i) stopping flow for a period of time; (ii) varying flow rate; and (iii) using two or more influent concentrations. The range of flow rates that are used in the following analyses is in the range of realistic values that can be employed using the stirred-flow chamber and they were tested to meet the assumption of a well-stirred chamber. The solution volume of the chamber is equal to that used by Carski and Sparks (1985) and Seyfried et al. (1989). The ratio of soil M/V_c cannot greatly exceed 1:5 to 1:10 in order to have a uniform suspension in the chamber and a constant flow rate with time (Seyfried et al., 1989). However, the ratio cannot be much smaller than this if one is to distinguish adsorption from the dilution process (Carski and Sparks, 1985). The influent-concentration range and the cation-exchange capacity that are of interest to us are similar to those found in soils. In the following discussion, three equations are used: a simple linear instantaneous model (Eq. [8]), the kinetic model (Eq. [10]) suggested by Seyfried et al. (1989), and a first-order model (Eq. [3b]). These three equations represent the three types of models that will be distinguished using the suggested experimental tests.

The first experimental test, stopping flow for a period of time, can help in distinguishing instantaneous equilibrium from time-dependent reactions (Seyfried et al., 1989). The assumption of this test is that, if nonequilibrium conditions exist, stopping flow for a sufficient time will allow the system to reach equilibrium. Thus, the ion concentration of the solution in the chamber should drop and, therefore, when the flow restarts, a drop in concentration will be measured when a kinetic model is employed but not for an instantaneous model (Seyfried et al., 1989). For an effective test, the flow must be stopped for at least the time required for 50% of the reaction to be complete. Seyfried et al. (1989) showed that, for $J = 0.83 \text{ mL min}^{-1}$, $V_c = 8.3 \text{ cm}^3$, $M = 1.6 \text{ g}$, and $E = 48.2 \text{ mmol kg}^{-1}$, the $t_{1/2}$ of the fastest reaction that can be distinguished from an instantaneous reaction is 0.3 min. Similarly, a $t_{1/2}$ greater than 60 min is also not distinguishable, but reactions that are very slow can be studied easily using batch techniques. Most exchange reactions in soils are rapid (Sparks, 1989). Consequently, the recommended stopping time for such systems is 15 to 60 min. The time increment during a continuous run for which flow is stopped is critical for the effectiveness of this test. Therefore, by comparing the predicted lines for the models expressed in Eq. [6] and [6a] with a continuous run, the maximum difference between the two models can be ascertained (Fig. 1). The stopped-flow test is most effective if the flow is stopped at this point. With any kinetic model, the flow has to be stopped prior to saturation of the adsorbent, which can occur with kinetic models like that in Eq. [3b] long before a steady state in solution concentra-

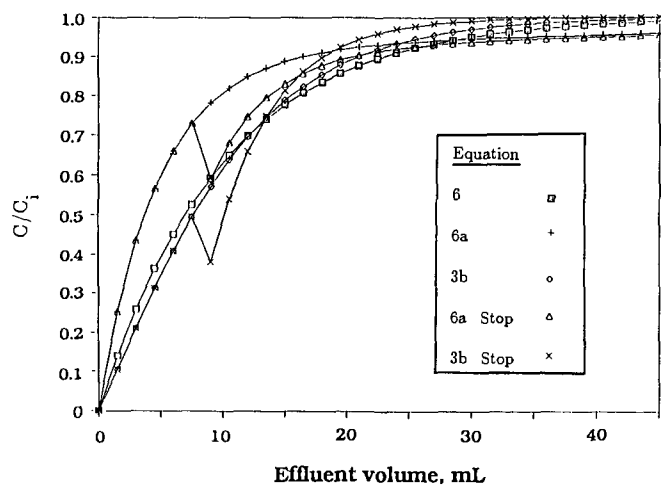


Fig. 1. Relative effluent concentration (C/C_i) as a function of effluent volume calculated for: instantaneous equilibrium (Eq. [6]) with calculated line showing results for continuous and stopped-flow runs (i.e., the results were identical for both runs); and kinetic models (Eq. [6a] and [3b]), for continuous and stopped (60 min of stopping flow after a 5-min reaction time) flow runs. Parameter values are: flow rate (J) = 1.5 mL min⁻¹, solution volume in chamber (V_c) = 5 mL, influent concentration (C_i) = 1 mol m⁻³, adsorbent mass (M) = 1 g, adsorption maximum (E) = 5 mmol kg⁻¹, apparent forward rate coefficient (k) = 0.023 min⁻¹, forward rate coefficient (k_f) = 0.2 min⁻¹, and reverse rate coefficient (k_r) = 0.01 min⁻¹.

tion is reached. Therefore, varying the time increment when the flow is stopped by conducting several stopped-flow tests helps to improve this test.

Calculated relative effluent concentration as a function of effluent volume, with and without stopping flow 5 min from the start of the reaction process for 60 min and using the three models (Eq. [6], [6a], and [3b]), are presented in Fig. 1. As expected, there is discontinuity in the curves for the two kinetics models when flow is stopped, unlike the smooth lines observed with the instantaneous-equilibrium model (Fig. 1). This discontinuity enables one to distinguish between the instantaneous-equilibrium models (Eq. [6]) and the two kinetics models (Eq. [3b] and [6a]) and provides the experimentalist with a simple tool to make such distinctions.

The second and third tests are combinations of experimental parameters (flow rates and influent concentrations) and appropriate presentation of the results. For example, presentations of effluent concentration as a function of time and also as a function of volume enables one to distinguish between instantaneous and kinetic processes (Fig. 2). Therefore, in the following discussion, both relative effluent concentration or adsorbed fraction vs. time or effluent volumes are used. Assuming instantaneous equilibrium and presenting relative concentration vs. time data, three distinct lines were obtained for three flow rates (Fig. 2a), while using effluent volume on the abscissa, the lines calculated for the three flow rates overlapped (Fig. 2b). This phenomenon, no effect of flow rate on relative concentration vs. effluent volume is specific to the instantaneous-equilibrium model and was not found for the two kinetics models (Fig. 3a and 3b).

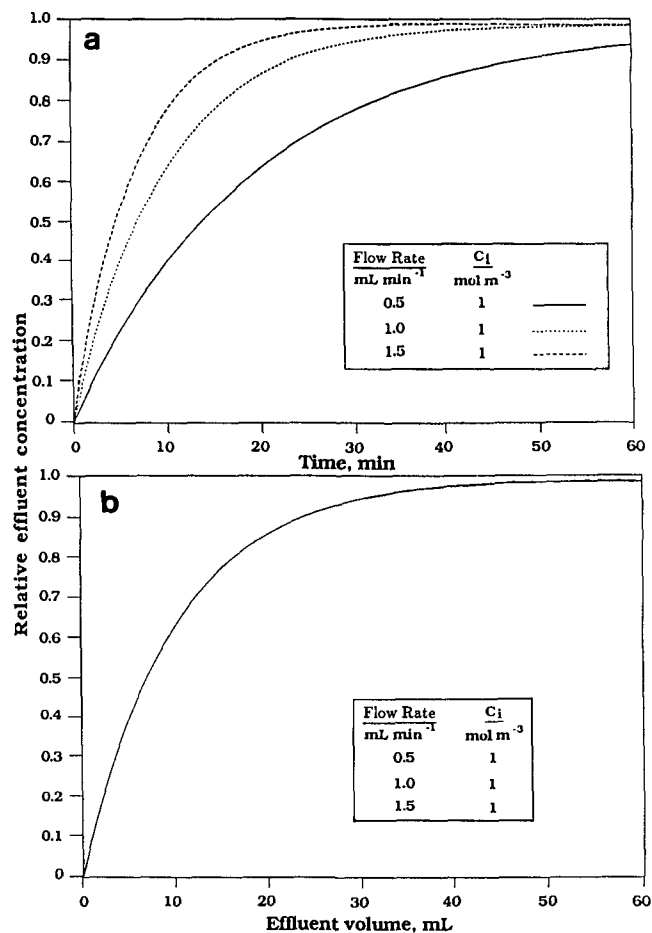


Fig. 2. Relative effluent concentration as a function of time (a) and effluent volume (b), using a numerical solution of a mass-balance equation (Eq. [1a]) in combination with an instantaneous-equilibrium model (Eq. [6]). Parameters values are solution volume in chamber (V_c) = 5 mL, adsorbent mass (M) = 1 g, adsorption maximum (E) = 5 mmol kg⁻¹.

Relative concentration as a function of volume is not affected by flow rate when instantaneous equilibrium is assumed, because adsorption is a function of the concentration, independent of time. Thus, a simple experimental method, i.e., varying flow rate, should be employed to distinguish between reaction rates that are measurable in the stirred-flow method and those that are not.

Producing the lines for Fig. 3b (a first-order kinetic model) revealed a problem that is common to models that are independent of solution concentration. Using the same rate coefficients for three simulated flow rates, negative concentration values were calculated for the slow-flow-rate line (0.5 mL min⁻¹) until 3.5 mL in Fig. 3b and, therefore, the line for the slow flow rate starts from 3.5 mL. Experimentally, this phenomenon is, of course, impossible for the initial condition at $t = 0$ and $S = 0$, but the determined first-order rate coefficient might be flow-rate dependent.

Influent-concentration and flow-rate tests using curves of adsorbed fraction as a function of time can be used to distinguish between kinetic reactions that are solution-concentration dependent and those that are solution-concentration independent (Fig. 4). The

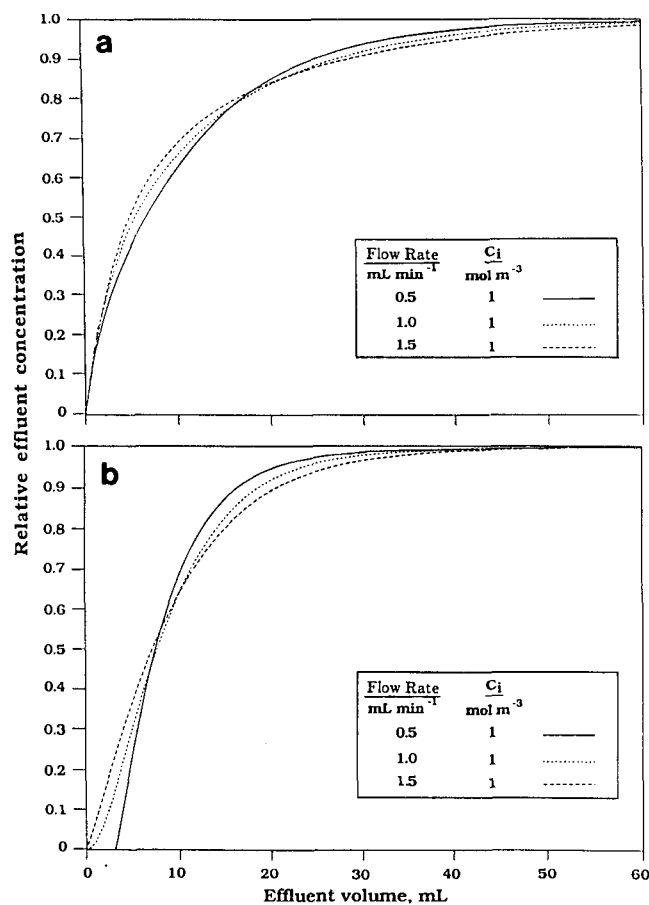


Fig. 3. Relative effluent concentration as a function of effluent volume, using a numerical solution of a mass-balance equation (Eq. [1a]) in combination with two kinetic models: (a) dependent on solution concentration (Eq. [6a]), and (b) not dependent on solution concentration (Eq. [3b]). Parameter values are solution volume in chamber (V_c) = 5 mL, adsorbent mass (M) = 1 g, adsorption maximum (E) = 5 mmol kg⁻¹, apparent forward rate coefficient (k) = 0.23 min⁻¹, forward rate coefficient (k_1) = 0.2 min⁻¹, and reverse rate coefficient (k_{-1}) = 0.01 min⁻¹.

first-order equation predicts that neither flow rate nor influent concentration will affect the lines describing adsorbed fractions (Fig. 4a). This stems from the assumption of this model that the rate of adsorption is not dependent on solution concentration. In the solution-dependent kinetic model, the adsorbed fraction as a function of time was affected by the flow rate and influent concentration (Fig. 4b). This is expected from the basic assumption of this model that the rate of adsorption is a function of time and solution concentration. Increasing flow rate enhances solution concentration as a function of time, which increases adsorbed quantity as a function of time. Thus, using the suggested experimental tests and properly presenting the data, one can distinguish between the models.

CONCLUSIONS

This study has outlined experimental procedures as well as mathematical analyses for studying kinetics of adsorption phenomena on clay minerals and soils using a stirred-flow method. A numerical solution of the mass-balance equation in combination with kinetic

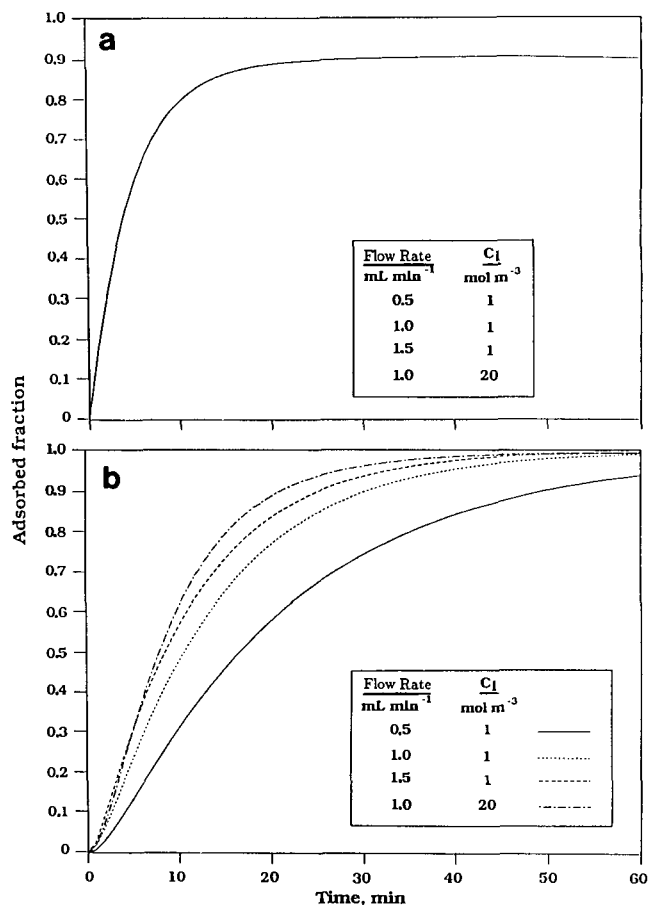


Fig. 4. Adsorbed fraction as a function of time, using a numerical solution of a mass-balance equation (Eq. [1a]) in combination with two kinetic models: (a) not dependent on solution concentration (Eq. [3b]), and (b) dependent on solution concentration (Eq. [6a]). Parameter values are solution volume in chamber (V_c) = 5 mL, adsorbent mass (M) = 1 g, adsorption maximum (E) = 5 mmol kg⁻¹, apparent forward rate coefficient (k) = 0.23 min⁻¹, forward rate coefficient (k_1) = 0.2 min⁻¹, and reverse rate coefficient (k_{-1}) = 0.01 min⁻¹.

and equilibrium models enables one to compare between different kinetic and equilibrium models. An instantaneous-equilibrium process can be confused with a kinetic phenomenon using a flow method. Therefore, instantaneous equilibrium must be ruled out before determining rate coefficients using the stirred-flow method or other flow methods. There is a need to distinguish between two main types of kinetic models: those that are dependent on solution concentration and those that are not. In order to distinguish between these types of models, three experimental tests were suggested: stopping the flow for at least 15 to 60 min, varying the flow rate, and using two or more influent concentrations.

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