

Kinetics and Mechanisms of Sulfate Adsorption/Desorption on Goethite Using Pressure-Jump Relaxation

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ABSTRACT

Sulfate adsorption/desorption on goethite (FeOOH) in aqueous suspension was investigated thermodynamically and kinetically. The SO_4 -adsorption isotherm indicated that adsorption decreased with increased pH of the goethite suspension. The triple-layer model fit the experimental data well when adsorbed SO_4 was assumed to be located at the β plane and held via outer-sphere complexation. Pressure-jump relaxation was used to determine the kinetics of SO_4 adsorption/desorption on goethite. A single relaxation was observed due to adsorption/desorption processes. Based on the equilibrium and kinetic studies, we hypothesized and tested two reaction mechanisms for SO_4 retention. The first postulated mechanism (Reaction 1) assumed that SO_4 was adsorbed on a positively charged surface site through electrostatic attraction. This mechanism was rejected because of the poor conformity between the intrinsic equilibrium constant ($K_{\text{eq}}^{\text{int}}$) determined from the static studies and that found from the ratio of forward (k_1^{int}) and backward (k_{-1}^{int}) rate constants, i.e., $K_1^{\text{int}} = k_1^{\text{int}}/k_{-1}^{\text{int}}$. It was found that the adsorption of SO_4 on goethite occurred simultaneously with the protonation of a neutral surface site, as assumed in the second hypothesized mechanism (Reaction 2). Based on this mechanism, a linear relationship between the reciprocal relaxation time (τ^{-1}) and various concentration terms was observed. From this relationship, k_2^{int} and k_{-2}^{int} were calculated and were $2.02 \times 10^8 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$ and 0.144 s^{-1} , respectively. The intrinsic equilibrium constant from kinetic measurements (K_2^{int}) was $10^{9.14} \text{ mol}^{-2} \text{ L}^2$, which was similar to the intrinsic equilibrium constant from the equilibrium studies, $10^{9.60}$.

ADSORPTION OF SO_4 on soils and soil constituents has been extensively studied, particularly as it affects various aspects of plant nutrition, soil acidity, soil salinity, and water quality. Many soils retain SO_4 , particularly those with high contents of Al and Fe oxides (Freney et al., 1962; Harward and Reisenauer, 1966). Hingston et al. (1972) showed that SO_4 adsorption on goethite and gibbsite decreased with an increase in pH up to 8, beyond which no further adsorption occurred. Similar results were found with soils (Harward and Reisenauer, 1966; Scott, 1976). Marsh et al. (1987) investigated the relationship between soil surface charge and SO_4 adsorption and found that a direct and very close relationship existed between positive surface charge and SO_4 adsorption. When positive surface charge was low, little or no SO_4 was sorbed by soils where the background electrolyte was NaCl or CaCl_2 .

Sulfate leaching in soils has been reported by a number of investigators, and is more extensive in soils that are low in Al and Fe oxides, particularly in the A ho-

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izons (Parfitt, 1978). Swoboda and Thomas (1965) found that SO_4 leaching occurred even in highly weathered soils that contained large amounts of Fe oxides, particularly if large volumes of water were applied to the soils. Sulfate leaching also can occur if positive sites on soils and soil constituents are blocked by organic ligands (for example, in highly organic soils), in part due to SO_4 having a lower binding constant than polycarboxylic acids (Haque and Walmsley, 1974). Thus, Gillman (1974) found more phosphate-extractable SO_4 in lower horizons where the point of zero charge (PZC) was higher and where there were more positive sites.

One of the possible mechanisms for SO_4 adsorption on soils and soil constituents is ligand exchange, whereby SO_4 replaces H_2O or OH groups from XOH_2 and XOH sites, where XOH_2 and XOH represent protonated and nonprotonated surface sites, respectively (Parfitt, 1978). Bornemesza and Llanos (1967) have also shown that OH ions are released during SO_4 adsorption. Parfitt and Russell (1977), Parfitt and Smart (1978) and Rajan (1978) showed that SO_4 is adsorbed by forming binuclear bridged complexes on Al and Fe oxides. Further evidence to support this mechanism was found by Martin and Smart (1987), who used x-ray photoelectron spectroscopy (XPS) to study SO_4 adsorption. Their results are consistent with those observed from infrared spectroscopy (IRS) studies by Parfitt and Smart (1978), who showed that an adsorbed SO_4 ion replaces two A-type OH groups (single coordinated to Fe^{3+} ions) on (100) and (010) goethite surface sites.

Hansmann and Anderson (1985), however, used electrophoresis to model SO_4 adsorption on goethite and found that SO_4 was weakly bound on the surface through electrostatic attraction. The intrinsic energy of SO_4 adsorption onto goethite was too low to allow significant binding. The adsorption behavior of SO_4 appeared different from phosphates and from SeO_3 , which are generally assumed to be adsorbed on oxides by ligand exchange. Ryden et al. (1987) reported that SO_4 did not have a detectable effect on PO_4 adsorption on hydrous ferric oxide gel, but other anions such as AsO_3 , SeO_3 , SiO_3 , and MoO_4 decreased PO_4 adsorption. Yates and Healy (1975) found that the rate and extent of SO_4 adsorption on ferric and chromic oxide/water interfaces were different from PO_4 , but similar to NO_3 , and concluded that SO_4 adsorption did not occur by a ligand-exchange process. However, the point of zero salt effect (PZSE) is shifted upward in a SO_4 background solution. These results illustrate, as Sposito (1984) pointed out, the "intermediate" surface complexation behavior of SO_4 . Arnold (1978) has reported that adsorption of SO_4 on a tropical soil resulted in an increase in the PZC of the soil. This would indicate that SO_4 is not located in the inner Helmholtz plane and so is not adsorbed by a ligand-exchange phenomenon. However, SO_4 is more strongly attracted to the surface than, say Cl under similar experimental conditions (Mott, 1981). Marsh et al. (1987) noted that the adsorption of SO_4 is not entirely nonspecific, for there is a strong selectivity of SO_4 over Cl. However,

they considered that electrostatic forces predominated for SO_4 /solid interactions.

Thus, the mechanism(s) of SO_4 adsorption on soils and soil constituents is not definitively understood. It is clear that macroscopic equilibrium studies are not suitable for determining adsorption mechanism(s). Spectroscopic studies provide direct information about adsorption mechanisms. However, previous SO_4 -adsorption studies employing spectroscopic techniques such as XPS and IRS are not appropriate, since the samples must first be subjected to desiccation and high-vacuum techniques. Johnston and Sposito (1987) have noted that harsh sampling techniques often eliminate or irreversibly alter the surface species of interest. Molecular-level information gleaned about the mechanisms, orientation, and dynamics of adsorbed species, obtained from experiments involving desiccation and high-vacuum treatments, may not be relevant to systems in a hydrated environment.

Few reports appear in the literature on the kinetics of SO_4 adsorption on soils and soil constituents (Sparks, 1989). Chang and Thomas (1963) studied SO_4 -adsorption kinetics on soils and minerals on a time scale of weeks. They suggested that the mechanism for SO_4 adsorption was ligand exchange. Rajan (1978) measured the rate of SO_4 adsorption on an Al oxide and the rate and amount of OH groups being released. He found that 90% of the reaction was complete in 10 min. Zhang et al. (1987) also studied SO_4 adsorption on soils using the same procedure as Rajan (1978), and they found a smaller ratio of OH/ SO_4 , compared with that observed by Rajan (1978) for oxides. They also found that the amount of OH released to the aqueous solution was much lower when SO_4 was adsorbed than when F was adsorbed. They concluded that information on the mechanism for SO_4 adsorption on oxides cannot be directly applied to soils because the activity, density, and distribution of the replaceable groups on the surface of an oxide may be quite different from those on the surfaces of soils.

Hodges and Johnson (1987) studied the kinetics of SO_4 adsorption and desorption on a soil using miscible-displacement and rapidly stirred batch procedures. They fitted data to a number of kinetic models to hypothesize the possible mechanism and the rate-controlling steps for the adsorption/desorption process. The rate coefficients were affected by the degree of mixing and by the flow rate, which led them to conclude that diffusion was the overall rate-limiting step. However, the authors concluded that the mechanism of SO_4 adsorption was not clear.

Lack of a suitable technique to measure the rate of SO_4 adsorption/desorption may be a major obstacle in understanding the mechanism of SO_4 retention on soils and soil constituents. Accordingly, we used a pressure-jump (p-jump) relaxation technique to determine the kinetics of SO_4 adsorption/desorption at the goethite/water interface. This technique, which can make measurements at millisecond and microsecond time scales, was previously used to ascertain the kinetics and mechanisms of molybdate adsorption/desorption on goethite (Zhang and Sparks, 1989). Results

from both thermodynamic and kinetic studies were used to ascertain the mechanism(s) for SO_4 adsorption/desorption.

MATERIALS AND METHODS

Sample Preparation

The goethite used in the study was synthesized in our laboratory following the procedure described by Atkinson et al. (1967). The freeze-dried sample was examined by x-ray diffraction and the characteristic 0.418-nm peak for goethite was observed. The goethite then was dialyzed in dialysis tubing until the conductivity of the suspension equalled that of deionized water. The particle size was $<2 \mu\text{m}$ after dispersion with an ultrasonic disperser.

The specific surface area of the goethite, which was measured using the ethylene glycol monoethyl ether adsorption method (Carter et al., 1986), was $70.1 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$. A potentiometric titration technique was employed to determine the surface site density of the goethite which was 6.4 site nm^{-2} . The determination was made using the nonlinear least squares optimization program FITEQL (Westall, 1982). The intrinsic equilibrium constants for the background electrolyte reactions on the surface ($\log K_{\text{Na}}^{\text{int}} = -8.80$ and $\log K_{\text{NO}_3}^{\text{int}} = 7.6$) were taken from Hayes and Leckie (1987). The intrinsic equilibrium constants for protonation ($\log K_{\text{a1}}^{\text{int}} = -5.80$) and deprotonation ($\log K_{\text{a2}}^{\text{int}} = -11.1$) were computed simultaneously with surface-site density using FITEQL, and were identical with those of Hayes and Leckie (1987).

Sodium nitrate and HNO_3 were used to adjust the ionic strength and pH, respectively, of the goethite suspension. Sodium sulfate was the adsorptive. All chemicals used were analytical reagent grade and no further purification was made.

Static Studies

The adsorption study was carried out by placing a goethite suspension containing a $2 \times 10^{-3} \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution, with NaNO_3 as the background electrolyte, into polypropylene centrifuge tubes. The final goethite particle concentration was 11.58 g L^{-1} and the ionic strength was 0.01 M . The tubes were shaken end-to-end on a reciprocating shaker overnight, centrifuged using a superspeed centrifuger (Sorvall RC-5B, Du Pont Instrument, Newtown, CT) at 34550 g for 30 min, and the supernatant solution was then filtered through $0.2\text{-}\mu\text{m}$ matrix membrane filter paper. Sulfate concentration was determined using ion chromatography, and the pH of the supernatant was measured.

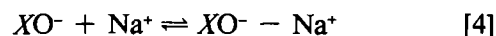
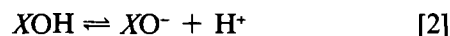
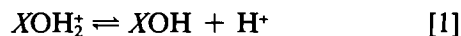
Kinetic Studies

In the kinetic studies, relaxation times (τ values) were measured for the SO_4 -goethite suspension at a 0.01 M ionic strength using a Dia-Log p-jump apparatus (DIA-RPC, Dia-Log Co.) and conductivity detector (DIA-RPM, Dia-Log Co.). During the p-jump relaxation measurement, 13.5 MPa of pressure was established on a cell containing the goethite and SO_4 suspension; then the pressure was released within $70 \mu\text{s}$ by bursting a brass membrane of 0.05-mm thickness. The reaction system was perturbed and a new equilibrium was established. The time required to reach the new equilibrium from the sudden pressure release is related to τ . The change in the reaction system was recorded as the change in conductivity, which reflected the concentration change in the reaction system during relaxation (Zhang and Sparks, 1989). A digitizer (DIA-RRC, Dia-Log Co.) was then triggered and the relative changes in conductivity between the suspension and the reference solution were recorded. The signals were then converted and transferred to a microcomputer for analysis. The final results of the relaxation could be read from the computer printout and displayed on an oscilloscope. The p-jump apparatus and the electrical conductivity detector were described in Zhang and Sparks (1989).

Application of Surface-Complexation Models

The constant-capacitance and modified-triple-layer models were used to describe SO_4 adsorption on goethite. The constant-capacitance model assumes that all adsorbed ions form inner-sphere complexes (Sposito, 1984). It has been successfully used to describe the adsorption of arsenate, borate, and phosphate on oxides and soils (Goldberg, 1986; Goldberg and Glaubig, 1986; Goldberg and Sposito, 1984a,b).

The triple-layer model (TLM) assumes that all adsorbed ions, except for H and OH, stay in the β plane and are adsorbed as outer-sphere complexes (Sposito, 1984). The following chemical reactions can be defined for the application of the TLM to SO_4 adsorption on goethite using the experimental conditions given above



where XOH represents 1 mol of reactive surface hydroxyl bound to an Fe ion in goethite. Equation [5] is the formation of an outer-sphere surface complex in which SO_4 ions are located at the β plane. The intrinsic conditional equilibrium constants for the previous reactions can be defined as:

$$K_{\text{a1}}^{\text{int}} = \frac{[\text{XOH}][\text{H}^+]}{[\text{XOH}_2]} \exp(-F\psi_\alpha/RT) \quad [6]$$

$$K_{\text{a2}}^{\text{int}} = \frac{[\text{XO}^-][\text{H}^+]}{[\text{XOH}]} \exp(-F\psi_\alpha/RT) \quad [7]$$

$$K_{\text{NO}_3}^{\text{int}} = \frac{[\text{XOH}_2^- - \text{NO}_3^-]}{[\text{XOH}_2][\text{NO}_3^-]} \exp(-F\psi_\beta/RT) \quad [8]$$

$$K_{\text{Na}}^{\text{int}} = \frac{[\text{XO}^- - \text{Na}^+]}{[\text{XO}^-][\text{Na}^+]} \exp(F\psi_\beta/RT) \quad [9]$$

$$K^{\text{int}} = \frac{[\text{XOH}_2^- - \text{SO}_4^{2-}]}{[\text{XOH}_2][\text{SO}_4^{2-}]} \exp(-2F\psi_\beta/RT) \quad [10]$$

where F is the Faraday constant, R is the universal gas constant, and T is the absolute temperature. Square brackets indicate concentration and the exponential terms represent the activity coefficients for a charged surface; where ψ_α and ψ_β are the electrical potentials at the α and β layer, respectively.

The surface-charge balance equations based on the above reactions are:

$$\sigma_\alpha = [\text{XOH}_2] + [\text{XOH}_2^- - \text{NO}_3^-] + [\text{XOH}_2^- - \text{SO}_4^{2-}] - [\text{XO}^-] - [\text{XO}^- - \text{Na}^+] \quad [11]$$

$$\sigma_\beta = [\text{XO}^- - \text{Na}^+] - 2[\text{XOH}_2^- - \text{SO}_4^{2-}] - [\text{XOH}_2^- - \text{NO}_3^-] \quad [12]$$

From the electroneutrality condition,

$$\sigma_\alpha + \sigma_\beta + \sigma_d = 0 \quad [13]$$

where σ_d is the charge at the diffusion layer; it can be calculated using Gouy-Chapman theory and the relationship

$$\sigma_d = -11.74C_s^{1/2} \sinh\left(\frac{F\psi_d}{2RT}\right) \quad [14]$$

where C_s is the concentration of a symmetrical monovalent electrolyte. The relation between charge and potential are derived, assuming that the planes can be treated as plates of two parallel-plate capacitors, with

$$\sigma_\alpha = C_1(\psi_\alpha - \psi_\beta) \text{ and} \quad [15]$$

$$-\sigma_d = C_2(\psi_\beta - \psi_d) \quad [16]$$

where C_1 and C_2 are the capacitance constants for the α - and β -plane layers, respectively, which cannot be measured experimentally. The values of C_1 and C_2 in this study are 1.2 and 0.2 F m⁻², respectively, and they were determined based on the goodness of the data fit to the TLM.

The TLM used in this study is modified from the original. A theoretical discussion and application of the modified TLM can be found in Hayes and Leckie (1986, 1987) and Zhang and Sparks (1989). In the modified TLM, SO₄ ions are allowed to form an inner-sphere surface coordination complex by placing them in the α layer such that



where XSO₄⁻ is the inner-sphere surface complex. The charge balance for the reactions in the α and β layer are then

$$\sigma_\alpha = [XOH_2^+] + [XOH_2^+ - NO_3^-] - [XSO_4^-] - [XO^-] - [XO^- - Na^+] \quad [18]$$

$$\sigma_\beta = [XO^- - Na^+] - [XOH_2^+ - NO_3^-] \quad [19]$$

In the case of SO₄ being adsorbed through an inner-sphere complex, the intrinsic conditional equilibrium constant would be

$$K^{int} = \frac{[XSO_4^-]}{[XOH_2^+][SO_4^{2-}]} \exp(-2F\psi_d/RT) \quad [20]$$

In the present study, parameters from both of the computed results when the adsorbed SO₄ ions are treated as an ion-pair (outer-sphere) surface complex or as a surface coordination (inner-sphere) complex were used to model the reactions thermodynamically and kinetically.

RESULTS AND DISCUSSION

Static Study

The isotherm for SO₄ adsorption on goethite is shown in Fig. 1. The adsorption of SO₄ was based on the difference between SO₄ concentration in the initial suspension and that in the supernatant solution after

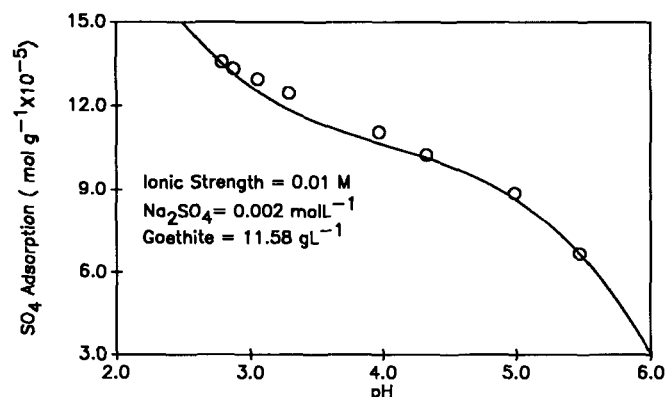


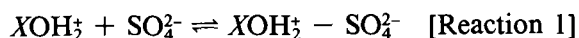
Fig. 1. Adsorption of SO₄ on goethite vs. pH. Experimental data are applied to the triple-layer model (TLM) assuming outer-sphere complexation. Symbols represent experimental data and the line represents the predicted relationship based on the TLM.

equilibrium. As pH increased, SO₄ adsorption decreased rapidly. The modified TLM was used to describe SO₄ adsorption on goethite for both inner- and outer-sphere complexation. For the outer-sphere case (Fig. 1), the predicted line agrees well with the experimental data. Although not shown, the data were not satisfactorily described when inner-sphere complexation was assumed to be operational. The constant-capacitance model did not successfully describe SO₄ adsorption on the goethite in this study. These findings would suggest that outer-sphere complexation or electrostatic attractions between SO₄ and the goethite surface predominate. This mechanism was confirmed by the p-jump relaxation studies.

Pressure-Jump Relaxation Studies

A single relaxation was observed with the direction of the relaxation signals indicating a decrease in the suspension conductivity of the suspensions during relaxation (Fig. 2). The τ^{-1} increased with increasing pH (Fig. 3), which may indicate that the relaxation was related to the proton concentration in the suspension. In preliminary experiments, relaxations were not observed in goethite-NaNO₃, goethite-HNO₃, HNO₃-NaNO₃, HNO₃-Na₂SO₄, or HNO₃-NaNO₃-Na₂SO₄ systems. These findings indicate that the relaxation observed was attributable to adsorption/desorption of SO₄ on the goethite surface.

If SO₄ adsorption on goethite occurs by electrostatic attraction or by outer-sphere complexation, two possible reaction mechanisms can be proposed:



where XOH₂⁺ - SO₄²⁻ represents a surface complex between a positively charged surface site and adsorbed SO₄ via electrostatic attraction. In Reaction 1, SO₄ is adsorbed on a protonated surface site that is positively charged. In Reaction 2, protonation and SO₄ adsorption on a neutral site occur simultaneously. The products of the two reactions are the same, thus it is impossible from equilibrium studies to determine which of the two reactions represents the correct mechanism. One way to ascertain the correct mechanism is to determine the consistency between kinetic and equi-

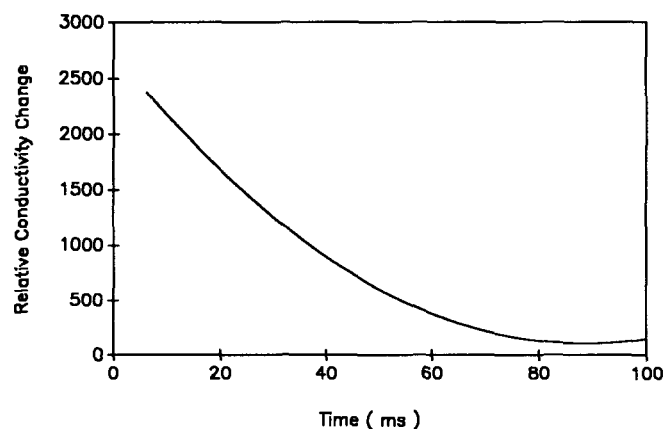


Fig. 2. Typical pressure-jump relaxation curve for the goethite suspension showing change in conductivity vs. time during the relaxation.

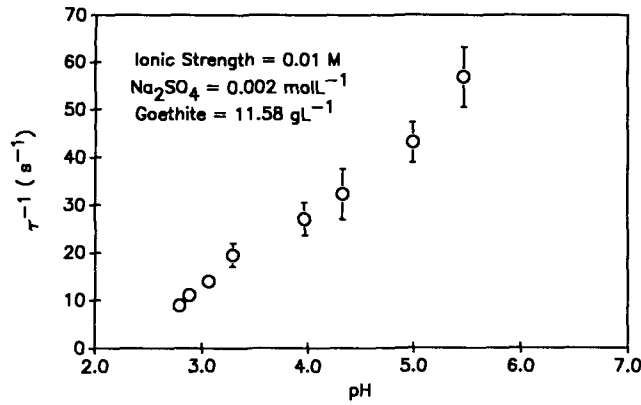


Fig. 3. Relationship between reciprocal relaxation times (τ^{-1}) and pH in the goethite suspension.

librium results for each reaction. The intrinsic equilibrium constants for the two reactions (K_1^{int} and K_2^{int} , respectively) can be written as

Reaction 1:

$$K_1^{\text{int}} = \frac{[\text{XOH}_2^+ - \text{SO}_4^{2-}]}{[\text{XOH}_2^+][\text{SO}_4^{2-}]} \exp\left(\frac{-2F\psi_\beta}{RT}\right) \quad [21]$$

Reaction 2:

$$K_2^{\text{int}} = \frac{[\text{XOH}_2^+ - \text{SO}_4^{2-}]}{[\text{XOH}][\text{H}^+][\text{SO}_4^{2-}]} \exp\left(\frac{F(\psi_\alpha - 2\psi_\beta)}{2RT}\right) \quad [22]$$

where the exponential terms in Eq. [21] and [22] represent the influence of surface potential on the conditional equilibrium constants, and are called the *activity coefficient* for the species in the suspension. One must also relate the surface potential to activation potentials for both the adsorption and desorption reactions. Defining the activation potentials as ψ_f^\ddagger and ψ_b^\ddagger for those required to overcome the electrical double layer (EDL) potential for the adsorption (forward) and desorption (backward) steps, respectively, and relating the intrinsic rate constants directly to the rate constants, one obtains

$$k_f^{\text{int}} = k_f \exp\left[\frac{F\psi_f^\ddagger}{RT}\right] \quad [23]$$

$$k_b^{\text{int}} = k_b \exp\left[\frac{F\psi_b^\ddagger}{RT}\right] \quad [24]$$

where k_f and k_b are the rate constants for the forward and backward reactions, respectively. The overall reaction constant is

$$K^{\text{int}} = \frac{k_f^{\text{int}}}{k_b^{\text{int}}} = \frac{k_f \exp\left[\frac{F\psi_f^\ddagger}{RT}\right]}{k_b \exp\left[\frac{F\psi_b^\ddagger}{RT}\right]} = K_1 \exp\left[\frac{F\psi_o}{RT}\right] \quad [25]$$

and

$$\frac{\exp\left(\frac{F\psi_f^\ddagger}{RT}\right)}{\exp\left(\frac{F\psi_b^\ddagger}{RT}\right)} = \exp\left(\frac{F\psi_o}{RT}\right) \quad [26]$$

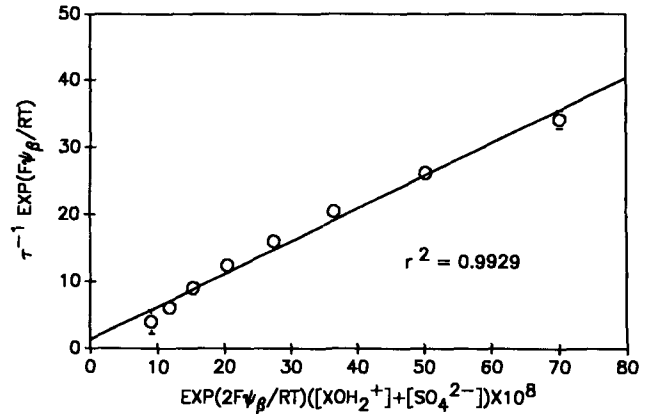


Fig. 4. Plot of the relationship between τ^{-1} with exponential and concentration terms as proposed in Eq. [30].

where ψ_o is the EDL potential for a specific reaction. In this study,

$$\psi_f^\ddagger = -\psi_b^\ddagger = \psi_o/2 = (\psi_\alpha - 2\psi_\beta)/2 \quad [27]$$

In arriving at Eq. [27], it is assumed that the magnitude of the activation potentials for adsorption and desorption are equal and opposite in sign. In this manner, the EDL properties are developed consistently for both equilibrium and kinetic analyses based on the TLM.

In the neighborhood of equilibrium, linearized relaxation-rate equations can be obtained (see derivations in the Appendix):

Reaction 1:

$$\tau^{-1} = k_1^{\text{int}} \exp\left(\frac{F\psi_\beta}{RT}\right) ([\text{XOH}_2^+] + [\text{SO}_4^{2-}]) + k_{-1}^{\text{int}} \exp\left(\frac{-F\psi_\beta}{RT}\right) \quad [28]$$

Reaction 2:

$$\tau^{-1} = k_2^{\text{int}} \exp\left(\frac{-F(\psi_\alpha - 2\psi_\beta)}{2RT}\right) ([\text{XOH}][\text{H}^+] + [\text{XOH}][\text{SO}_4^{2-}] + [\text{H}^+][\text{SO}_4^{2-}]) + k_{-2}^{\text{int}} \exp\left(\frac{F(\psi_\alpha - 2\psi_\beta)}{2RT}\right) \quad [29]$$

where k_1^{int} , k_{-1}^{int} , k_2^{int} , and k_{-2}^{int} are the intrinsic forward and backward rate constants for Reaction 1 and 2, respectively. Rearranging Eq. [28] and [29], one obtains

$$\tau^{-1} \exp\left(\frac{F\psi_\beta}{RT}\right) = k_1^{\text{int}} \left\{ \exp\left(\frac{2F\psi_\beta}{RT}\right) ([\text{XOH}_2^+] + [\text{SO}_4^{2-}]) \right\} + k_{-1}^{\text{int}} \quad [30]$$

$$\tau^{-1} \exp\left(\frac{-F(\psi_\alpha - 2\psi_\beta)}{2RT}\right) = k_2^{\text{int}} \left\{ \exp\left(\frac{-F(\psi_\alpha - 2\psi_\beta)}{RT}\right) ([\text{XOH}][\text{H}^+] + [\text{XOH}][\text{SO}_4^{2-}] + [\text{SO}_4^{2-}][\text{H}^+]) \right\} + k_{-2}^{\text{int}} \quad [31]$$

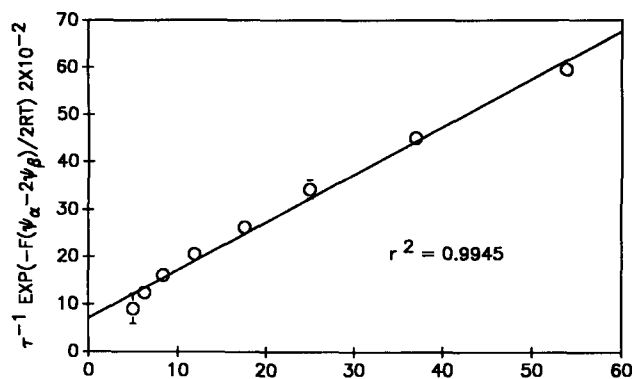


Fig. 5. Plot of the relationship between τ^{-1} with exponential and concentration terms as proposed in Eq. [31].

Equations [30] and [31] represent the linearized relationships between the reciprocal relaxation times, the exponential terms and the concentration terms. If a suggested mechanism is consistent with the experimental relaxation data, then a plot of τ^{-1} with the exponential term on the left-hand side of Eq. [30] and [31] vs. the expression in the brackets on the right-hand side of Eq. [30] or [31] will give a straight line with a slope of k_1^{int} and an intercept of k_1^{int} if Reaction 1 is operational or k_2^{int} and k_2^{int} if Reaction 2 is applicable. For each pH at which the kinetic experiments were run, values for ψ_α , ψ_β , and reactant and product concentrations, as determined from the equilibrium studies, were inserted into Eq. [30] and [31]. As shown in Fig. 4 and 5, Eq. [30] and [31] both produce straight lines indicating that both Reaction 1 and 2 are operational. Intrinsic equilibrium constants for both reactions were calculated using the ratios of $k_1^{\text{int}}/k_1^{\text{int}}$ ($4.239 \times 10^7 \text{ mol}^{-1} \text{ L s}^{-1}/3.137 \text{ s}^{-1}$) and $k_2^{\text{int}}/k_2^{\text{int}}$ (see Table 1). The forward and backward intrinsic rate constants were calculated from the slope and intercept, respectively, of Fig. 4 and 5. The values obtained were $\log K_1^{\text{int}} = 7.13$ and $\log K_2^{\text{int}} = 9.14$. The $\log K_{\text{eq}}^{\text{int}}$ obtained from the static study was 9.6. Thus, K_2^{int} is of similar magnitude to $K_{\text{eq}}^{\text{int}}$ (Table 1). Based on the consistency between equilibrium and kinetic results, Reaction 2 is the most plausible mechanism for SO_4 adsorption on goethite.

The pH of an oxide suspension increases when SO_4 is added, or a certain amount of acid must be added to maintain the pH. Based on this, some investigators have concluded that SO_4 is adsorbed via ligand exchange (Parfitt, 1978; Rajan, 1978). As was mentioned above, there has not been direct evidence that OH is released from the hydrated surface site. The increase in OH concentration during adsorption may be caused by dissociation of H_2O ; H^+ can then be consumed by two processes. One way is through the reaction given in Eq. [31]. The other possible mechanism is the protonation of the anion itself, especially at high anion concentrations (Davis and Leckie, 1980). Both of these processes would yield OH, causing an increase in pH.

CONCLUSIONS

Based on the findings of this study, the mechanism for SO_4 adsorption on goethite is adsorption of SO_4

Table 1. Intrinsic rate and equilibrium constants for Reaction 2 determined from kinetic and equilibrium measurements.

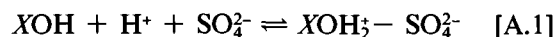
k_2^{int}	k_2^{int}	$\text{Log} K_2^{\text{int}\dagger}$	$\text{Log} K_{\text{eq}}^{\text{int}\dagger}$
$\text{mol}^{-2} \text{L}^2 \text{s}^{-1}$	s^{-1}		
2.02×10^8	0.144	9.14	9.60

$\dagger K_2^{\text{int}}$ is the intrinsic equilibrium constant determined from the ratio of the rate constants i.e., $k_2^{\text{int}}/k_2^{\text{int}}$; $K_{\text{eq}}^{\text{int}}$ is the intrinsic equilibrium constant determined from equilibrium (static) measurements.

on a neutral site that is simultaneously protonated. Adsorption on goethite results in the formation of an outer-sphere surface complex via electrostatic attraction. The adsorption process occurs very rapidly and desorption is the rate-limiting step. By using a kinetic method such as p-jump, we should ultimately be able to better understand the kinetics and mechanisms of ion adsorption/desorption on the surface of soils and soil constituents. Many of these reactions are very rapid, and they cannot be measured using most traditional batch and flow techniques. Studies such as this will, in turn, lead to better predictive models for ion retention/mobility in soils, which will assist us in preserving environmental quality and in more efficiently applying plant nutrients to soils.

APPENDIX

The relationship between the inverse of the relaxation time constant, τ , and the concentration of the reacting species shown in Eq. [29] can be developed as follows. The same procedure can be used to derive the relationship in Eq. [28]. For the reaction



the rate is defined as

$$r = -\frac{d[\text{XOH}]}{dt} = -\frac{d[\text{SO}_4^{2-}]}{dt} = -\frac{d[\text{H}^+]}{dt} = \frac{d[\text{XOH}_2^+ - \text{SO}_4^{2-}]}{dt} \quad [\text{A.2}]$$

or

$$r = -k_f[\text{XOH}][\text{SO}_4^{2-}][\text{H}^+] + k_b[\text{XOH}_2^+ - \text{SO}_4^{2-}] \quad [\text{A.3}]$$

where t is time, k_f and k_b are the rate constants for the forward and backward reactions, respectively, and the terms in the brackets are the time-dependent concentrations. At equilibrium, $r = 0$ and Eq. [A.3] becomes

$$0 = -k_f[\overline{\text{XOH}}][\overline{\text{SO}_4^{2-}}][\overline{\text{H}^+}] + k_b[\overline{\text{XOH}_2^+ - \text{SO}_4^{2-}}] \quad [\text{A.4}]$$

where the overbar denotes the equilibrium concentration. Relating this to the law of mass action,

$$\frac{[\overline{\text{XOH}_2^+ - \text{SO}_4^{2-}}]}{[\overline{\text{XOH}}][\overline{\text{SO}_4^{2-}}][\overline{\text{H}^+}]} = \frac{k_f}{k_b} = K_1 \quad [\text{A.5}]$$

Following a small perturbation, e.g., a pressure-jump, equilibrium concentrations are shifted a small amount, x . According to the conservation-of-mass law, the time-dependent concentrations are

$$[\text{XOH}] = [\overline{\text{XOH}}] + x \quad [\text{A.6.1}]$$

$$[\text{SO}_4^{2-}] = [\overline{\text{SO}_4^{2-}}] + x \quad [\text{A.6.2}]$$

$$[\text{H}^+] = [\overline{\text{H}^+}] + x \quad [\text{A.6.3}]$$

$$[\text{XOH}_2^+ - \text{SO}_4^{2-}] = [\overline{\text{XOH}_2^+ - \text{SO}_4^{2-}}] - x \quad [\text{A.6.4}]$$

Substituting Eq. [A.6.1]–[A.6.4] into Eq. [A.3],

$$r = \frac{dx}{dt} = -k_f([\overline{\text{XOH}}] + x)([\overline{\text{SO}_4^{2-}}] + x) \\ + ([\overline{\text{H}^+}] + x) + k_b([\overline{\text{XOH}_2^+} - \overline{\text{SO}_4^{2-}}] - x) \\ = -k_f[\overline{\text{XOH}}][\overline{\text{SO}_4^{2-}}][\overline{\text{H}^+}] + k_b[\overline{\text{XOH}_2^+} - \overline{\text{SO}_4^{2-}}] \\ - k_f([\overline{\text{XOH}}][\overline{\text{SO}_4^{2-}}] + [\overline{\text{XOH}}][\overline{\text{H}^+}]) \\ + [\overline{\text{SO}_4^{2-}}][\overline{\text{H}^+}]x - k_f([\overline{\text{XOH}}] + [\overline{\text{SO}_4^{2-}}]) \\ + [\overline{\text{H}^+}]x^2 - k_f x^3 - k_b x \quad \text{[A.7]}$$

The first two terms vanish because of Eq. [A.4], creating

$$\frac{dx}{dt} = -(k_f[\overline{\text{XOH}}][\overline{\text{SO}_4^{2-}}] + [\overline{\text{XOH}}][\overline{\text{H}^+}]) \\ + [\overline{\text{SO}_4^{2-}}][\overline{\text{H}^+}] + k_b)x \\ - k_f([\overline{\text{XOH}}] + [\overline{\text{SO}_4^{2-}}] + [\overline{\text{H}^+}])x^2 - k_f x^3 \quad \text{[A.8]}$$

which can be further simplified if only small equilibrium perturbations are considered, i.e., small x . Then the last two terms become vanishingly small, leading to

$$\frac{dx}{dt} = -(k_f[\overline{\text{XOH}}][\overline{\text{SO}_4^{2-}}] + [\overline{\text{XOH}}][\overline{\text{H}^+}]) \\ + [\overline{\text{SO}_4^{2-}}][\overline{\text{H}^+}] + k_b)x \quad \text{[A.9]}$$

One can define

$$\frac{dx}{dt} = -\frac{1}{\tau} x \quad \text{[A.10]}$$

where

$$\tau^{-1} = k_f([\overline{\text{XOH}}][\overline{\text{SO}_4^{2-}}] + [\overline{\text{XOH}}][\overline{\text{H}^+}]) \\ + [\overline{\text{SO}_4^{2-}}][\overline{\text{H}^+}] + k_b \quad \text{[A.11]}$$

Combining the following relationships based on Eq. [23] and [24],

$$k_f^{\text{int}} = k_f \exp\left(\frac{F(\psi_\alpha - 2\psi_\beta)}{2RT}\right) \quad \text{[A.12]}$$

and

$$k_b^{\text{int}} = k_b \exp\left(\frac{-F(\psi_\alpha - 2\psi_\beta)}{2RT}\right) \quad \text{[A.13]}$$

Eq. [A.11] becomes,

$$\tau^{-1} = k_f^{\text{int}} \exp\left(\frac{-F(\psi_\alpha - 2\psi_\beta)}{2RT}\right) ([\overline{\text{XOH}}][\overline{\text{SO}_4^{2-}}] + [\overline{\text{XOH}}][\overline{\text{H}^+}]) \\ + [\overline{\text{SO}_4^{2-}}][\overline{\text{H}^+}] + k_b^{\text{int}} \exp\left(\frac{F(\psi_\alpha - 2\psi_\beta)}{2RT}\right) \quad \text{[A.14]}$$

Eq. [A.14] is the same as Eq. [29] when one considers that the concentration terms here are the equilibrium concentrations

$$\tau^{-1} = k_f^{\text{int}} \exp\left(\frac{-F(\psi_\alpha - 2\psi_\beta)}{2RT}\right) ([\overline{\text{XOH}}][\overline{\text{H}^+}] + [\overline{\text{XOH}}][\overline{\text{SO}_4^{2-}}]) \\ + [\overline{\text{H}^+}][\overline{\text{SO}_4^{2-}}] + k_b^{\text{int}} \exp\left(\frac{F(\psi_\alpha - 2\psi_\beta)}{2RT}\right) \quad \text{[A.15]}$$

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