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Evaluation of contaminant ion adsorption/ desorption on goethite using pressure-jump relaxation kinetics

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Abstract

The adsorption/desorption of contaminant ions on soil constituents such as metal oxides occurs within milliseconds. The rapid kinetics of Cu^{2+} and arsenate adsorption/desorption on goethite ($\alpha\text{-FeOOH}$) were investigated using the pressure-jump (p-jump) relaxation technique, which provides rate constants and mechanistic information for fast reactions. Results of p-jump experiments at 25°C revealed that both Cu^{2+} and arsenate were specifically adsorbed on goethite. The divalent copper ion formed an inner-sphere monodentate surface complex, while arsenate formed an inner-sphere bidentate surface complex with goethite. In both cases, the rate constants for the adsorption reactions exceeded those for desorption, indicating that the desorption of Cu^{2+} and arsenate from the goethite surface was the rate-limiting process. Pressure-jump relaxation techniques can be used to predict the adsorption behavior of heavy metals in soil environments.

1. Introduction

There is considerable concern regarding trace element contamination of soils and sediments. Trace elements are defined as chemical elements whose indigenous concentrations (either in the solid or aqueous phase) are less than 100 ppm (Jurinak and Tanji, 1993). These pollutants are potentially hazardous to plant, animal and human health. The sources of contamination include the disposal of industrial wastes, application of pesticides and sewage sludges, mining industry and smelting by-products. In the past, the disposal of trace element wastes often failed to consider their potential as environmental contaminants. There is now the recognition that proper disposal and clean-up methods require a better understanding of the interactions between toxins and soils.

Sorption by soils and sediments is one of the most important processes controlling trace element levels in natural waters. Significant quantities of these compounds are adsorbed onto the surfaces of soil constituents such as Fe- and Al-oxides, clays, carbonates and organic matter. This process is extremely rapid and occurs within milliseconds (Amacher, 1991; Sparks and Zhang, 1991). Even though surface adsorption reactions occur rapidly in comparison with other chemical processes in natural environments, kinetic studies can help determine the mechanisms underlying ion adsorption on oxides (Sparks, 1989). However, conclusive mechanistic information can only be obtained in conjunction with spectroscopic experiments and adsorption modeling. Understanding the fate of inorganic contaminants in the environment requires knowledge of their interactions with the soil solid matrix, e.g., do these ions specifically bind to surface functional groups or is adsorption due to electrostatic interactions with the oxide surface? Specific adsorption is often described as the formation of inner-sphere surface complexes, which would involve the loss of at least one water molecule from the primary hydration sphere surrounding the ion, resulting in direct binding of the ion to a surface functional group. If the attraction is electrostatic, the ion maintains its primary hydration sphere when it forms an outer-sphere surface complex. Inner-sphere surface complex bonds are either covalent or ionic and they are much stronger than outer-sphere surface complexes (Sposito, 1984).

Conventional kinetic techniques, such as batch methods, cannot be used to measure the rapid rates of ion adsorption reactions. However, relaxation methods, specifically pressure-jump (p-jump) relaxation, have been successfully employed to measure the kinetics of ion adsorption/desorption reactions on soil constituents (Yasunaga and Ikeda, 1986; Sparks and Zhang, 1991). The p-jump technique is especially useful because it simultaneously supplies rate information for both adsorption and desorption processes. The p-jump method is based upon the fact that the equilibrium constant for a chemical reaction is dependent upon pressure and can be expressed by the relationship:

$$\left(\frac{\delta \ln K}{\delta \ln P}\right)_T = -\frac{\Delta V}{RT} \quad (1)$$

where K is the chemical equilibrium constant, P is the pressure, ΔV is the standard molar volume change of the reaction, R is the universal gas constant, and T is the absolute temperature (Bernasconi, 1976). Therefore, a pressure perturbation shifts the equilibrium state of a chemical reaction. The system must then relax to the final equilibrium state. The relaxation is a function of all the elementary reaction steps that comprise the chemical reaction.

The use of p-jump relaxation to measure the kinetics of ion adsorption/desorption on metal oxide surfaces was pioneered by several Japanese chemists (Yasunaga and Ikeda, 1986). Their research includes some of the following adsorption/desorption kinetic studies: proton interactions with TiO_2 (Ashida et al., 1978) and Fe-oxide surfaces (Astumian et al., 1981), divalent metal ion (Hachiya et al., 1984) and uranyl (Mikami et al., 1983a) reactions with $\gamma\text{-Al}_2\text{O}_3$ surfaces, and phosphate (Mikami et al., 1983b) and chromate (Mikami et al., 1983c) adsorption reactions on $\gamma\text{-Al}_2\text{O}_3$. Hayes and Leckie (1986) were the first to use p-jump relaxation kinetics to study the adsorption/desorption behavior of a metal ion contaminant (Pb^{2+}) on goethite ($\alpha\text{-FeOOH}$). Other successive studies monitored the rapid adsorption/desorption kinetics of molybdate (Zhang and Sparks, 1989), sulfate (Zhang

and Sparks, 1990a, b), selenate and selenite (Zhang and Sparks, 1990a, b) and Cu^{2+} (Grossl et al., 1994) on goethite.

This paper focuses on two pressure-jump relaxation kinetic studies that examine the adsorption behavior of Cu^{2+} and arsenate, an oxyanion, on goethite ($\alpha\text{-FeOOH}$). Goethite was chosen because it is the most widespread of the Fe-oxides in natural environments and the most stable in the pH range (4 to 9) of most soil systems (Schwertmann and Taylor, 1989). It is also widely used as a model for laboratory systems due to its well characterized surface chemistry and crystal morphology (Schwertmann and Cornell, 1991). The information gleaned from these investigations will help elucidate the fate of Cu^{2+} and arsenate in natural environments that are rich in Fe-oxide reactive surfaces.

2. Materials and methods

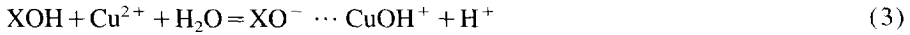
2.1. Sample preparation

The samples used for the p-jump kinetic studies were obtained from the same lot as those used for equilibrium adsorption studies. Sample preparation involved equilibrating a given concentration of the adsorptive (the ion in solution that has the potential of being adsorbed) with a specific quantity of the adsorbent (solid surface on which adsorption occurs) at a given pH. The adsorptives were the cation Cu^{2+} and the As(V) oxyanion, arsenate. The adsorbent for both of these studies was goethite. In the first study 0.785 M Cu^{2+} , as $\text{Cu}(\text{NO}_3)_2$, was equilibrated with a 10 g l^{-1} suspension of goethite in the presence of 0.01 and 0.005 M NaNO_3 , added as a background electrolyte. In the second study, 1 mM arsenate, as sodium arsenate was equilibrated with the same quantity of goethite and with 0.01 and 0.1 M NaNO_3 . All reactants were prepared using American Chemical Society reagent grade chemicals.

The goethite was synthesized in our laboratory using the method described by Schwertmann and Cornell (1991). It was characterized by X-ray diffraction analysis, and transmission electron microscopy and scanning electron microscopy to ensure the goethite's purity. The surface area of the goethite was equal to $50 \text{ m}^2 \text{ g}^{-1}$ determined from a triple point N_2 -Brunauer-Emmett-Teller (BET) adsorption isotherm.

Samples were prepared in a flat-bottomed water-jacketed reaction vessel covered with a removable Plexiglas lid containing entry ports for a stirrer, a pH electrode and burette tip. The goethite suspensions together with the adsorptive and background electrolyte were mixed with an overhead driven polyethylene propeller stirrer spinning at about 5.0 revolutions per second. After the desired pH was reached, by dropwise addition of 0.2 M HNO_3 or NaOH , 20 ml of the suspension was removed and transferred to 50 ml polypropylene centrifuge tubes which were placed on a reciprocating shaker ($180 \text{ cycles min}^{-1}$) for 24 hours. Subsequently, the pH of the sample was checked for any drift and, if necessary, pH was readjusted to the desired value. Half of the sample (10 ml) was then set aside to be used for p-jump experiments. The remaining 10 ml were centrifuged at 20,000g, the supernatant filtered through 0.2 micron filters and analyzed for Cu or As by inductively coupled plasma spectrometry.

The modified triple layer model (TLM) (Hayes and Leckie, 1986) was used to simulate the adsorption of Cu^{2+} on goethite. The formation of both inner- and outer-sphere surface complexes were considered and are represented by the following reactions:



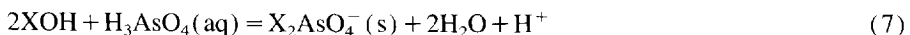
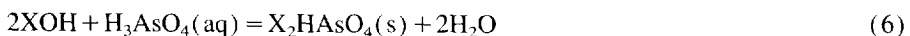
where XOH describes a neutral site on the goethite surface and Eq. (2) portrays the formation of an inner-sphere surface complex while Eq. (3) indicates the formation of an outer-sphere complex. The intrinsic conditional equilibrium constants for Eqs. (2) and (3) are expressed as:

$$K_{\text{is}}(\text{int}) = \frac{[\text{XOCu}^+][\text{H}^+]}{[\text{XOH}][\text{Cu}^{2+}]} \exp\left(\frac{-F\psi_0}{RT}\right) \quad (4)$$

$$K_{\text{os}}(\text{int}) = \frac{[\text{XO}^- \cdots \text{CuOH}^+][\text{H}^+]}{[\text{XOH}][\text{Cu}^{2+}]} \exp\left(\frac{-F(\psi_\beta - \psi_\alpha)}{RT}\right) \quad (5)$$

where brackets indicate concentrations, F is the Faraday constant, R is the universal gas constant, T is the absolute temperature, and ψ is the surface potential for the α and β planes. The α plane contains ions that have formed an inner-sphere surface configuration and the β plane contains ions that are adsorbed to the surface as outer-sphere complexes. The surface complexation modeling for the adsorption of Cu^{2+} on goethite is described in greater detail by Grossl et al. (1994), which includes all surface hydrolysis reactions, background electrolyte surface reactions, and lists all the necessary modeling parameters. The nonlinear least-squares optimization program, FITEQL (Westall, 1982) was used to compute intrinsic equilibrium constants for the formation of Cu/goethite surface complexes (Eqs. 4 and 5), surface species concentrations, and surface charge and potentials from the adsorption titration data.

The constant capacitance model (CCM) (Stumm et al., 1980) was used to examine the adsorption of arsenate on goethite. The CCM assumes that adsorbing ions form inner-sphere surface complexes. We used the CCM to predict the adsorption of arsenate on goethite as both mono- and bidentate surface species. The surface site density used for CCM calculations was $2.3 \text{ sites nm}^{-2}$, which was determined from arsenate adsorption isotherms conducted at constant pH values of 6.0 and 6.8 and initial arsenate concentrations of 0.25 to 3 mM. The surface reactions defining the adsorption of arsenate as monodentate surface complexes were the same as those presented by Goldberg (1986). We also used the intrinsic conditional equilibrium constants for surface protonation/deprotonation reactions and the capacitance value ($C = 1.06 \text{ F m}^{-2}$) given by Goldberg (1986). The bidentate ligand exchange surface reactions were represented as:



The corresponding intrinsic conditional equilibrium expressions for the formation of bidentate surfaces complexes were defined as:

$$K_{As}^1(\text{int}) = \frac{[X_2HAsO_4]}{[XOH]^2[H_3AsO_4]} \quad (8)$$

$$K_{As}^2(\text{int}) = \frac{[X_2AsO_4^-][H^+]}{[XOH]^2[H_3AsO_4]} \exp\left(\frac{-F\psi_o}{RT}\right) \quad (9)$$

Again, FITEQL version 3.1 (Herbelin and Westall, 1994) was used to fit the intrinsic surface complexation constants (Eqs. 8 and 9) to the experimental equilibrium adsorption data. The program was also used to compute the concentrations of surface species needed for kinetic evaluation of As adsorption/desorption on goethite.

The p-jump instrument used for our studies was manufactured by the DIA-LOG Company located in Düsseldorf, Germany. It is similar in design to the apparatus described in detail by Knoche (1975, 1986). To conduct a p-jump experiment it was necessary that during the course of an experiment (~ 1 hour) particle settling was kept to a minimum. Consequently, sample suspensions were sonified at least one hour prior to data collection. In fact, the greatest limitation of using the p-jump technique for metal sorption investigations is that it is restricted to the use of very pure, high surface area materials.

Typically, a p-jump experiment was performed by filling a sample electrode cell with the suspension equilibrated with the adsorptive at a selected pH. For the Cu^{2+} studies, p-jump experiments were run in the pH range 4.0 to 6.0. For the arsenate investigations, the pH range for the kinetic experiments was from 6.0 to 8.0. The filtered supernatant of the equilibrated suspensions were then added to the reference electrode cell. These cells have small electrodes built into their inner wall that monitor the conductivity changes occurring during the course of a relaxation experiment. Each of these cells has a capacity of about 1 ml. The laden cells were then covered with a thin Teflon membrane and tightly sealed. These cells were inserted into the pressure autoclave which comprises one part of the whole pressure-jump apparatus, the other part being a system for conductivity detection (Fig. 1). The Teflon membrane cover constitutes a portion of the inner wall of the pressure chamber. The chamber is sealed with a thin strip of brass foil that is specifically milled to burst once the pressure within the chamber reaches approximately 13.5 MPa. Pressure was applied to the autoclave by forcing water into the chamber with a hand operated mechanical pump. Pressure changes were transmitted to the sample suspension and reference solutions via the Teflon membrane.

The pressure perturbation is attained by increasing the pressure until the brass foil bursts and the pressure instantaneously (~ 60 ms) drops to ambient conditions. The sample equilibrated at the higher pressure (13.5 MPa) must now relax to the new equilibrium established at ambient pressure. The relaxation information is monitored by the conductivity detection system (Fig. 1), which is comprised of a wheatstone bridge, a digitizer, oscilloscope, and a personal computer containing a data evaluation software program. The sample and reference electrode cells are linked to and comprise two arms of the wheatstone bridge. The other two arms are made up of variable resistors and capacitors which are adjusted to balance the bridge using the oscilloscope as a viewing screen. The bridge is balanced at ambient conditions and becomes unbalanced upon pressurization. Thus, after the brass foil ruptures, a piezoelectric capacitor triggers collection of the relaxation event which is recorded as the voltage change associated with the bridge returning to the balanced state.

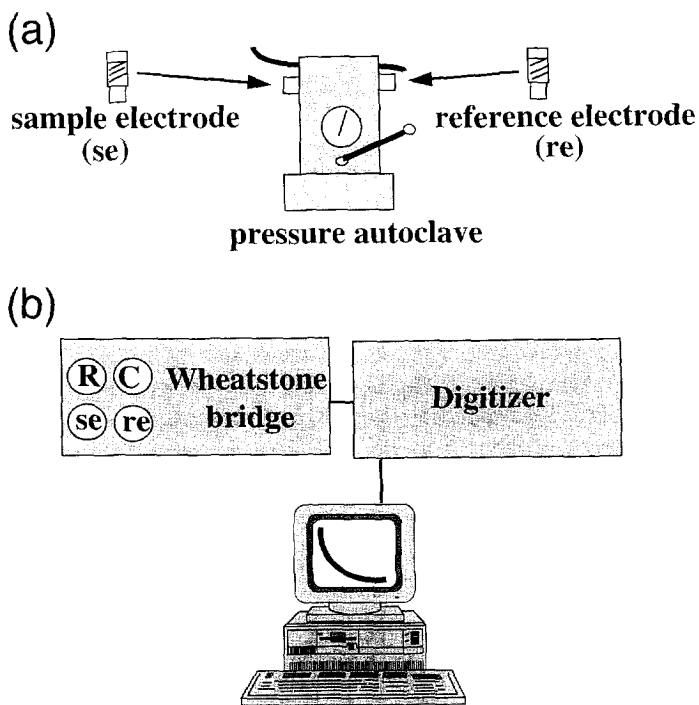


Fig. 1. Schematic of the pressure-jump apparatus. (a) Pressure induction system, (b) conductivity detection system. The letters R and C represent variable resistors and capacitors, respectively.

This information is then digitized and relayed to a microcomputer, where the relaxation curve is immediately displayed on the computer monitor. The information is plotted as the relative amplitude of the relaxation as a function of time in seconds.

The computer contains a software program provided by the manufacturer that allows for quick and direct computation of relaxation time constants or τ (tau). Tau is defined as the time it takes the relaxation to reach $1/e$ of the initial amplitude. The data evaluation program calculates τ by fitting and comparing the experimentally derived relaxation curve to a series of polynomial equations.

To ensure that the signals we were evaluating were only due to ion adsorption/desorption reactions, we also conducted p-jump experiments under identical conditions, however, in the absence of either Cu^{2+} or arsenate on goethite. When these were omitted no interfering relaxation signals were observed.

3. Results and discussion

3.1. Adsorption/desorption of Cu(II) on goethite

Equilibrium adsorption data reveals that adsorption of Cu^{2+} onto goethite increased from 6% at pH 3.5 to almost 100% at pH 6.0 (Fig. 2). The greatest increase in adsorption occurred between pH 4.5 and 5.5. The results were consistent with others (Benjamin and

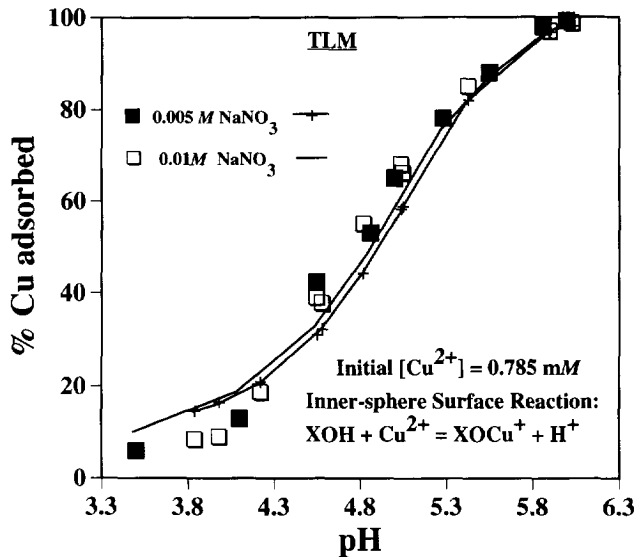
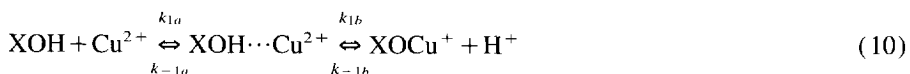


Fig. 2. Equilibrium adsorption data for Cu(II) adsorption on goethite as a function of pH.

Leckie, 1981; Hayes, 1987; Stumm, 1992) investigating divalent metal ion adsorption on oxides. There was no distinct difference between adsorption edges run at different background electrolyte concentrations. This would suggest that Cu^{2+} is specifically adsorbed to the goethite surface and not adsorbed through an electrostatic interaction. Additionally, modified TLM simulations of Cu(II) adsorption onto goethite as a monodentate inner-sphere surface complex agreed nicely with the experimental data (Fig. 2), while outer-sphere calculations (not shown here) were incompatible with the experimental results.

The kinetic experiments were conducted in the pH range 4.5 to 6.0, the range associated with the greatest increase in Cu^{2+} adsorption. It was also in this pH range that we were confident that the observed relaxations were the result of Cu^{2+} adsorption/desorption on goethite. Below this range it was difficult to resolve if the relaxations were due to Cu^{2+} adsorption or to surface hydrolysis reactions on goethite. Above pH 6.0, Cu^{2+} begins to precipitate as copper hydroxide. The rate of the relaxation times decreased with increasing pH along the adsorption edge (Fig. 3), for example τ measured at pH 4.8 was 40 ms and decreased to 10 ms at pH 5.95.

We postulated that Cu^{2+} is adsorbed to the goethite surface forming an inner-sphere monodentate surface complex (Grossl et al., 1994). Previous p-jump studies investigating the adsorption behavior of divalent metal ions on $\gamma\text{-Al}_2\text{O}_3$ (Hachiya et al., 1984) and Pb^{2+} on goethite (Hayes, 1987) were successfully able to fit their kinetic data to a model originally developed by Eigen and Tamm (1962) to describe metal complex formation in homogeneous systems. When this model is applied to a heterogeneous system, such as ours, it assumes that Cu^{2+} forms a steady state intermediate prior to the formation of an inner-sphere monodentate surface complex and can be represented as:



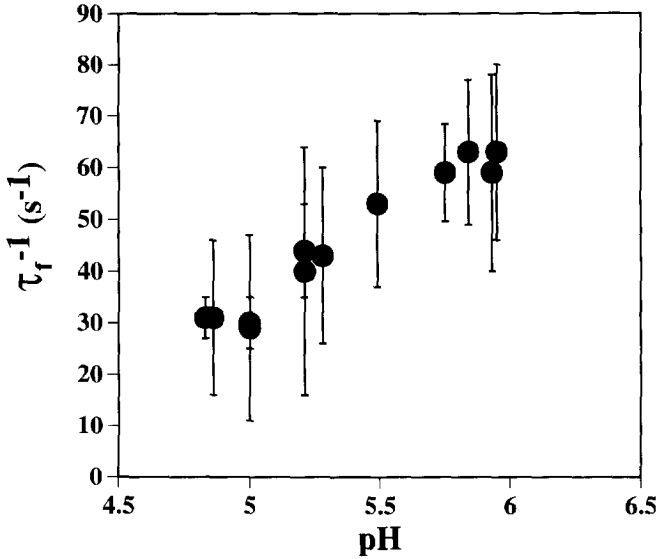


Fig. 3. τ^{-1} as a function of pH for Cu(II) adsorption/desorption on goethite.

where XOH represents a neutral surface site on goethite, k_{1a} and k_{1b} are forward rate constants, and k_{-1a} and k_{-1b} are reverse rate constants. To determine if our kinetic results were consistent with this proposed mechanism, it was necessary to derive a linearized rate equation that related τ^{-1} to the concentration of reactive species in Eq. (10). The final derived expression was:

$$\tau^{-1} = k_{-1a} \left[\{ [\text{XOCu}^+] + [\text{H}^+] \} + K^{\text{int}} \exp\left(\frac{-F\psi_0}{RT}\right) \{ [\text{XOH}] + [\text{Cu}^{2+}] \} \right] \quad (11)$$

where K^{int} ($10^{1.9}$) is the intrinsic equilibrium constant for the formation of a monodentate Cu/goethite surface complex. The intrinsic equilibrium constant, surface potentials, and species concentrations were obtained from modified TLM calculations and FITEQL. The entire concentration term on the right side of Eq. (3) can be symbolized as CT, to yield the simplifying relationship:

$$\tau^{-1} = k_{-1a}(\text{CT}) \quad (12)$$

The plot of τ^{-1} as a function of CT forced through the origin was linear with $r^2 = 0.92$ (Fig. 4). Thus, the mechanism described by Eq. (10) is indeed plausible. The rate constant for the desorption process (k_{-1a}) was calculated from the slope of the regression line and equal to $10^{4.88} \text{ l mol}^{-1} \text{ s}^{-1}$. Consequently, it was possible to calculate the rate constant for Cu^{2+} adsorption (k_{1a}) onto goethite, which was equal to $10^{6.81} \text{ l mol}^{-1} \text{ s}^{-1}$. For more detailed information regarding the derivation of Eq. (11), and determination of the forward and reverse rate constants readers should refer to Hachiya et al. (1984), Hayes (1987) and Grossl et al. (1994).

It should be noted that for all Cu^{2+} adsorption experiments a double relaxation was actually observed. However, only the fast τ was evaluated by the linearized rate equation and used to calculate the rate constants presented above. The slower τ values ranged from

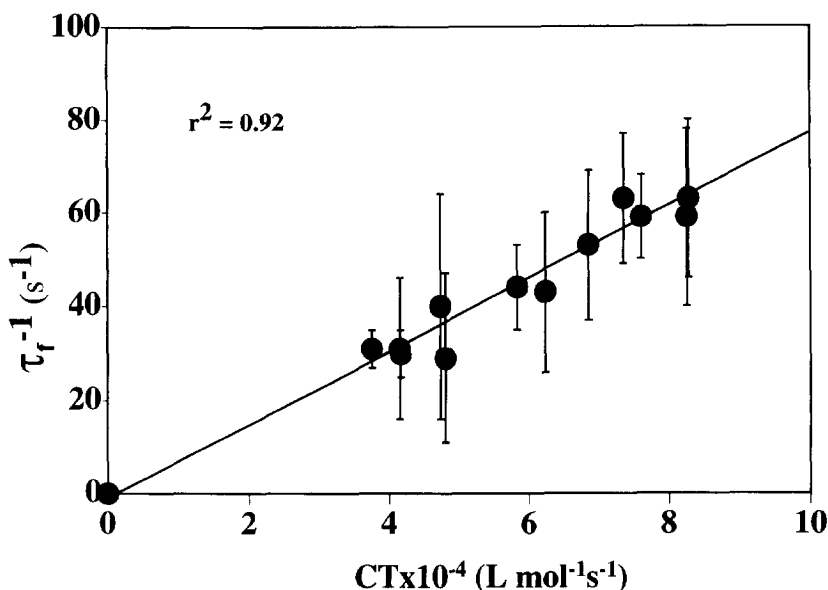


Fig. 4. τ^{-1} as a function of the concentration term for Cu(II) adsorption/desorption on goethite.

100 to 500 ms and were about one order of magnitude slower than the fast τ values. Unfortunately, we were unsuccessful at determining a mechanism for the slower set of τ values. We speculate that the mechanism responsible for the slower relaxation is one proposed by Benjamin and Leckie (1981) and Hachiya et al. (1984) who suggested that metal ions were adsorbed on surface sites with different binding affinities. The goethite surface is comprised of three different types of surface hydroxyl functional groups. One of the functional groups is singly, one is doubly, and another is triply coordinated to Fe^{3+} . There are equal quantities of the singly and doubly coordinated groups on the goethite surface, each comprising 43% of the total number of functional group sites (Hiemstra et al., 1989). The remaining number of sites ($\sim 14\%$) are triply coordinated to Fe^{3+} . In the pH range of our study (4.0 to 6.0), it is the doubly coordinated sites that are in the neutral form (Hiemstra et al., 1989) and, therefore, we believe have a greater affinity for Cu^{2+} ions. Consequently, the adsorption of Cu^{2+} on these sites may be responsible for the signal associated with the faster τ values, whereas, the slower values may result from the adsorption of Cu^{2+} on the singly and triply coordinated hydroxyls.

The adsorption/desorption of numerous divalent metal ions (Mn^{2+} , Pb^{2+} , Cu^{2+} , Zn^{2+} , and Co^{2+}) onto $\gamma\text{-Al}_2\text{O}_3$ was investigated by Hachiya et al. (1984) using pressure-jump relaxation kinetics. These investigators used the Eigen and Tamm steady-state model and found that these metals were adsorbed onto the alumina surface forming inner-sphere monodentate surface complexes. Interestingly, they related the rate of adsorption of these metal ions onto the alumina surface to the rate of water release from the primary hydration sphere of these metal ions. The relationship between the intrinsic rate constants for divalent metal ion adsorption determined by Hachiya et al. (1984) and between the rate constants for water exchange was linear (Wehrli et al., 1990; Stumm, 1992). Similarly, we wanted to establish if the adsorption of divalent metal ions on goethite followed the same relationship

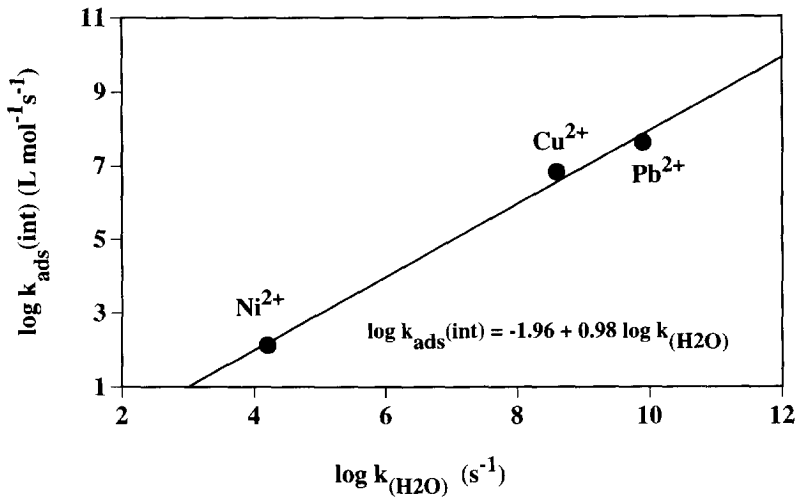


Fig. 5. The log of the rate constants for adsorption of Cu^{2+} , Pb^{2+} , and Ni^{2+} on goethite as a function of the log of the rate constants for water exchange from the primary hydration sphere of these respective cations.

presented above. We used the data from our study (Grossl et al., 1994), and data investigating Pb^{2+} (Hayes, 1987) and Ni^{2+} (Mehadi, 1993) adsorption on goethite. These three investigations, consistent in the use of surface (modified TLM) and kinetic modeling (steady-state intermediate; Eigen and Tamm, 1962), all concluded that the divalent metal ions formed monodentate inner-sphere surface complexes with the goethite surface. The intrinsic log of the rate constants for adsorption were plotted versus the log of the rate constants for removal of a coordinated water molecule encompassing each of the ions (Fig. 5). Although the plot consisted of only three points the relationship between water exchange seemed to be linearly coordinated to the intrinsic adsorption kinetics on goethite and followed the same trend observed for the alumina systems discussed earlier. The relationship for goethite could be expressed by:

$$\log k_{\text{ads(int)}} = -1.96 + 0.98 \log k_{\text{(H}_2\text{O)}} \quad (13)$$

The slope of this relationship is almost unity; therefore, the formation of an inner-sphere surface complex requires the loss of one of the water molecules from the primary hydration sphere of the metal ion. As a result, if the detachment rate of the water molecule is slow then the adsorption of the metal ion will also be slow.

3.2. Arsenate adsorption/desorption on goethite

The amount of arsenate adsorbed on goethite decreased from about 95 to 60 mmol kg^{-1} as pH increased from 6.0 to 11.0 (Fig. 6). These results are consistent with other equilibrium studies investigating arsenate adsorption on goethite, and are typical for oxyanion adsorption on goethite (Hingston et al., 1971; Goldberg, 1986). There was no difference between adsorption edges measured with background electrolyte concentrations of 0.01 and 0.1 M NaNO_3 (Fig. 6). This suggests that arsenate forms an inner-sphere surface complex with goethite. Recent X-ray absorption fine structure (XAFS) spectroscopic studies (Waychunas

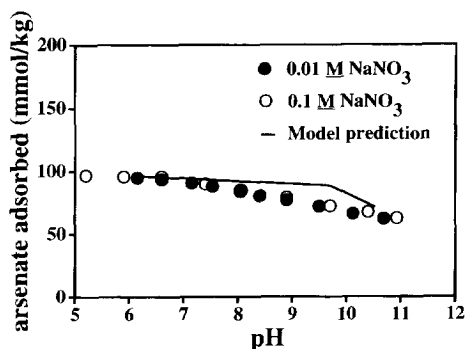


Fig. 6. Equilibrium adsorption data for arsenate adsorption on goethite versus pH.

et al., 1993; Fendorf et al., 1993) indicate that arsenate predominately forms inner-sphere bidentate surface complexes with goethite. Consequently, we used the CCM to simulate arsenate adsorption as an inner-sphere bidentate surface complex. Overall, the simulations fit the experimental data, except in the pH range from about 8.0 to 10.0, where the predicted values were higher than experimental values (Fig. 6). The intrinsic equilibrium constants for Eqs. (8) and (9), computed using FITEQL, were $10^{17.0}$ and $10^{11.4}$, respectively.

Pressure-jump relaxation experiments were evaluated over the pH range 6.5 to 7.5. In this pH range, we were able to confidently associate the relaxation signals with arsenate adsorption/desorption. We observed a double relaxation event for arsenate adsorption/desorption on goethite (Fig. 7). The faster τ values increased from about 10 to 20 ms with increasing pH, whereas the slow τ values remained constant at about 50 ms.

We propose that the mechanism for arsenate adsorption on goethite is a two-step process resulting in the formation of an inner-sphere bidentate surface complex (Fig. 8). The first step involves an initial ligand exchange reaction of H_2AsO_4^- (aq) with goethite, which forms an inner-sphere monodentate surface complex. We believe that this step produces the signals associated with the fast τ values. The next step involves a second ligand exchange reaction, resulting in the formation of an inner-sphere bidentate surface complex. This step produces the signals associated with the slow τ values.

To judge if the mechanism portrayed in Fig. 8 was plausible and consistent with our kinetic data, we used the following linearized rate equations relating τ^{-1} values to the concentrations of reactive species:

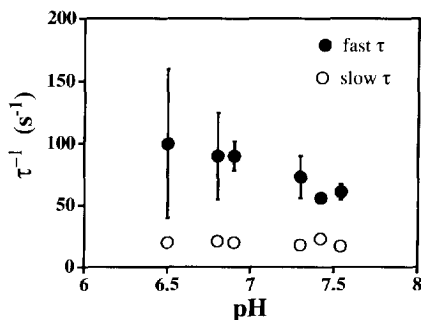


Fig. 7. Fast and slow τ^{-1} values versus pH for arsenate adsorption/desorption on goethite.

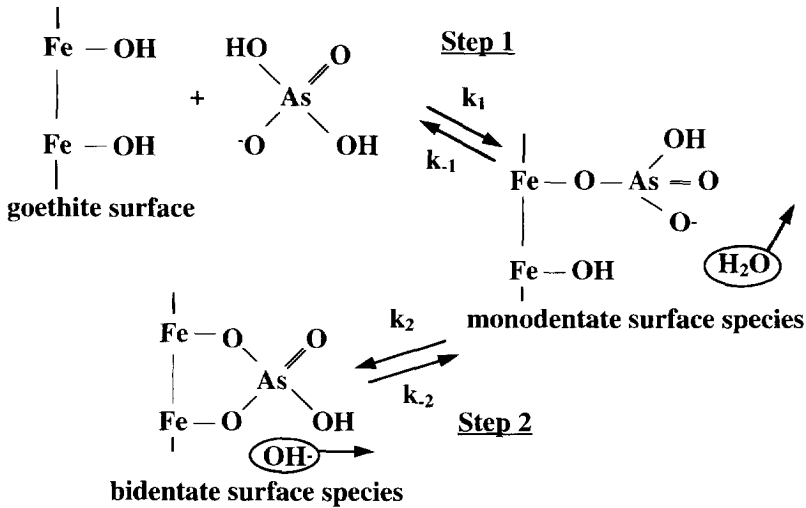


Fig. 8. Proposed mechanism for arsenate adsorption/desorption on goethite.

$$\tau_f^{-1} + \tau_s^{-1} = k_1([\text{XOH}] + [\text{H}_2\text{AsO}_4^-]) + k_{-1} + k_2 + k_{-2} \quad (14)$$

$$\tau_f^{-1} \cdot \tau_s^{-1} = k_1[k_2 + k_{-2}]\{[\text{XOH}] + [\text{H}_2\text{AsO}_4^-]\} + k_{-1}k_{-2} \quad (15)$$

The derivation for these equations was acquired from Bernasconi (1976) and is based on the two-step reaction system ($A + B \leftrightarrow C \leftrightarrow D$). Thus, plots of $\tau_f^{-1} + \tau_s^{-1}$ and $\tau_f^{-1} \cdot \tau_s^{-1}$ as a function of the concentration term ($[\text{XOH}] + [\text{H}_2\text{AsO}_4^-]$) should be linear if the mechanism depicted in Fig. 8 is probable. The charts were linear (Fig. 9) suggesting that our proposed mechanism was plausible. From these plots (Fig. 9), it was possible to determine the rate constants for adsorption and desorption reactions for both steps (Fig. 8), where $k_1 = \text{slope (Fig. 9A)}$, $k_{-1} = \text{intercept (Fig. 9A)} - \text{slope (Fig. 9B)}/\text{slope (Fig. 9A)}$, $k_2 = \text{intercept (Fig. 9A)} - k_{-1} - k_{-2}$, and $k_{-2} = \text{intercept (Fig. 9B)}/k_{-1}$. The calculated values for the rate constants were $k_1 = 1.8 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$, $k_{-1} = 9 \text{ s}^{-1}$, $k_2 = 14 \text{ s}^{-1}$, and $k_{-2} = 8 \text{ s}^{-1}$. The rate of the reverse reactions, associated with the breaking of arsenate/goethite bonds, were slower than the forward reactions and therefore the rate limiting steps. Having determined the rate constants for all the reactions involved in our proposed mech-

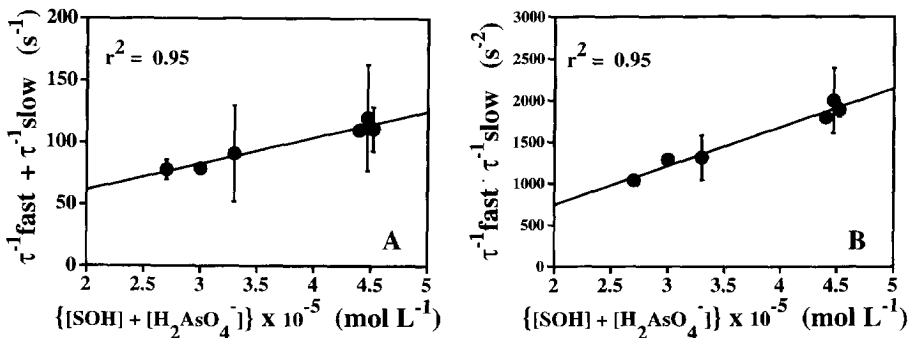


Fig. 9. Evaluation of linearized rate equations (Eqs. 14 and 15) for the mechanism displayed in Fig. 8.

anism (Fig. 8) it was possible to calculate the equilibrium constants for steps 1 and 2 from the relationship:

$$K_{\text{eq}} = k_{\text{forward}}/k_{\text{reverse}} \quad (16)$$

The equilibrium constant for step 1 was $10^{5.31}$ and K_{eq} for step 2 was $10^{0.26}$. Hence, the adsorption of arsenate and subsequent formation of the innersphere bidentate arsenate/goethite surface complex is thermodynamically favorable.

The kinetically determined equilibrium constant for the overall formation of the bidentate arsenate/goethite surface complex ($K_{\text{step 1}} \times K_{\text{step 2}} = 10^{5.57}$) was much smaller than that calculated using the CCM ($10^{19.2}$). Yet, the kinetically determined value for the formation of the monodentate surface complex (step 1) was consistent with K (int) values for the same reaction calculated with the CCM (Goldberg, 1986 and this study), which suggests that the mechanism proposed for step 1 is valid. However, step 2 may involve more elementary reactions than are illustrated in Fig. 8, which increase the overall equilibrium constant. This is a reasonable assumption, since the p-jump apparatus can monitor only reactions that generate measurable changes in conductivity. If step 2 involves other elementary surface reactions not detected using p-jump, our proposed mechanism (Fig. 8) may not be complete. The development of sophisticated new spectroscopic and microscopic surface probes may resolve this issue. Nonetheless, based on our kinetic and equilibrium adsorption studies and on spectroscopic evidence (Fendorf et al., 1993; Waychunas et al., 1993), arsenate appears to form an inner-sphere bidentate surface complex with goethite.

4. Conclusions

In natural environments inorganic metal contaminants are extensively sorbed on soil constituents such as Fe-oxides. The adsorption of metals on oxides occurs within milliseconds, too rapidly to be measured by conventional batch techniques. However, the kinetics of metal adsorption/desorption reactions on oxides was investigated using a pressure-jump relaxation technique, which determined rate constants for adsorption and desorption processes and provided mechanistic information regarding these reactions. Our results suggested that both Cu^{2+} and arsenate were specifically adsorbed on goethite. The Cu^{2+} ion formed an inner-sphere monodentate surface complex and arsenate formed an inner-sphere bidentate surface complex with goethite. The rate constants for desorption processes were smaller than those for the adsorption of both Cu^{2+} and arsenate on goethite, and desorption can be considered rate-limiting. Information from these experiments can help predict the adsorption behavior and ultimate fate of polluting ions in natural systems composed predominately of Fe-oxide surfaces.

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