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Surface coverage effects on the desorption kinetics of selenite from a hydroxyaluminum–montmorillonite complex

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A B S T R A C T

Information on the desorption of metals and metalloids from soils and clays are essential for a better understanding of their mobility, transport, and fate in natural environments. We investigated nitrate-, phosphate-, and citrate-induced desorption kinetics of preadsorbed selenite (presented as Se henceforth) from a hydroxyaluminum–montmorillonite (HyA–Mt) complex at three different surface coverages of 8%, 25%, and 69% of its Langmuir predicted adsorption maximum (262.61 mmole kg^{-1}). Generally the mole fraction of preadsorbed Se released after the attainment of desorption equilibrium was significantly higher with increasing surface coverage. Desorption kinetics of Se from the clay was best described by the Elovich model. The Elovich model parameter β representing the rate of Se desorption increased as the surface coverage increased. Both kinetic data and mole fraction of Se released at desorption equilibrium supported the contention that adsorption bond strength progressively decreases with increasing surface coverage. Both citrate and phosphate remobilized Se at significantly faster rates than nitrate at any surface coverage level. Citrate showed a significantly faster rate of Se release than phosphate only at 8% surface coverage but not at 25% and 69% surface coverages, suggesting that differential ability of these two ligands to influence the kinetics of Se release was also surface coverage dependant. The findings of the present study would help better understand the consequences of different surface coverages on soil colloids by preadsorbed Se as well as the impacts of phosphate fertilization and rhizospheric processes in influencing Se mobility in soil and related environments.

1. Introduction

Selenium is a trace element of special concern in the environment because of the dual importance of its essentiality and toxicity to animal and human health. Selenium is an essential nutrient for maintaining animal and human health, and an intake of 0.01–0.3 mg Se kg^{-1} diet is generally considered adequate [1]. Selenium is also considered to be one of the most toxic elements in the earth's crust [2]. An intake of 5–15 mg Se kg^{-1} diet (or higher) over a period of time can cause acute or chronic toxicity symptoms [1]. This small range in concentration in which Se behaves as both an essential nutrient and a toxic trace element emphasizes the essentiality of studying the processes that govern its transport, bioavailability, and fate in the environment.

In soils, sediments, and associated environments, the transport, bioavailability, and fate of trace elements including Se are largely dictated by the adsorption–desorption reactions at the particle–water interface. Adsorption of Se onto various natural and synthetic adsorbents has been studied extensively [3–19]. But the kinetics and mechanisms of the desorption of trace elements including Se from soils and clays have been largely obscure, even after repeated emphasis on its essentiality to a better understanding of the mobility, transport, and fate of trace elements in natural environments. Indeed, a great need in the adsorption research requires more research on the desorption phenomena [20].

It is recognized that the affinity/strength of adsorption of an adsorbate on an adsorbent decreases as the surface excess of the adsorbate increases. One of the principal determinants of the desorption pattern of an adsorbed species from a colloidal surface is the strength of adsorption, which is principally dictated by the adsorption mechanisms, such as the type of surface complex formed, surface orientation, multinuclearity, adsorption bond distance, and bond disorder. Apart from the charge and surface properties of the adsorbent, the type of adsorbate, ionic environments, and residence time, the mechanisms of adsorption are also largely influenced by the level of surface coverages. This has been demonstrated for a few oxyanions by elucidating the molecular scale mechanisms of their adsorption on inorganic soil colloids [21–27]. On the basis of a pressure-jump relaxation study and confirmed by extended X-ray absorption fine structure (EXAFS), Grossl et al. [25] and Fendorf et al. [24] demonstrated that arsenate can

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form three types of surface complexes on goethite depending on the surface coverage level. For arsenate adsorption on goethite, the XAFS data reported by Fendorf et al. [24] indicated that monodentate surface complexes (R = interatomic distance; $R_{\text{As–Fe}}$ = 3.59 Å) dominated at low surface coverages, bidentate mononuclear complexes ($R_{\text{As–Fe}}$ = 2.85 Å) dominated at high surface coverages, and bidentate binuclear complexes ($R_{\text{As–Fe}}$ = 3.24 Å) dominated at surface coverages near monolayer capacity. Fendorf et al. [24] also reported very similar results for chromate adsorption on the same sample. Grossl et al. [25] proposed that at extremely low surface coverages, a ligand exchange reaction of H_2AsO_4- with surface OH groups formed the monodentate complex. At high surface loadings, the adsorption of arsenate was dominated by the formation of bidentate surface complex after a second ligand exchange reaction occurred. For arsenate adsorption on a ferrihydrite, Waychunas et al. [28] discovered a As–Fe bond distance ($R_{\text{As–Fe}}$) of 3.29 ± 0.04 Å which indicated binuclear bridging for most of their samples. However, their sample with the lowest arsenate loading (Γ = As/Fe molar ratio; log $\Gamma = -2.82$) gave the $R_{\text{As–Fe}}$ value of 3.65 Å, which corresponds to a monodentate arsenate complex. In a study concerning competitive adsorption of arsenate and phosphate on an Andisol, Violante and Pigna [29] observed that inhibition of arsenate adsorption by the presence of phosphate at varying phosphate to arsenate molar ratios (0.2–2.0) in the bathing solutions was different for different targeted surface coverages by arsenate. Inhibition of arsenate adsorption by the presence of phosphate was several times higher when 100% and 70% surface coverages by arsenate were targeted as compared to when the target surface coverage by arsenate was 35%.

As there is convincing evidence in the literature that adsorption mechanisms of the oxyanions change to varying degrees depending on the levels of surface coverage, the desorption kinetics of an oxyanion from an adsorbent must be significantly affected by its amount preadsorbed on the surface of the adsorbent (i.e., the surface coverage). However, little is known on the influence of surface coverage of adsorbates on their desorption kinetics. Studies on the desorption kinetics of the environmentally important oxyanions from soils and clays in relation to varying extents of surface coverage are essential to address the natural soils and sediments with varying contaminant loads. Indeed this is one of the least researched areas in sorption–desorption phenomena. This paper reports the nitrate-, phosphate-, and citrate-induced desorption kinetics of Se from a hydroxyaluminum–montmorillonite (HyA–Mt) complex having different levels of surface coverage of preadsorbed Se. This clay has been chosen, since HyA interlayers/coatings on Mt and vermiculites (Vt) are very common in acid to slightly acid soils [30–33]. Phosphate and nitrate were included as desorptive solutions because they are common nutrient ions in soil solutions. Citrate was chosen as a desorptive agent, since it is one of the major organic ligands in the rhizosphere [34–36]. This study addresses the consequences of dual factors on the desorption phenomena: (1) the relationship between the levels of surface coverage by the preadsorbed Se and subsequent desorption kinetics of Se and (2) the influence of different desorptive solutions on the Se desorption kinetics. Such an understanding is necessary to provide much needed information on the mobility and fate of Se in the environment.

2. Materials and methods

2.1. Preparation of hydroxyaluminum (HyA)–montmorillonite (Mt) complex

The term, HyA–Mt complex, used in this paper indicates HyA interlayered and coated Mt. The preparation methods and characteristics of the HyA–Mt are briefly discussed below. For a more detailed discussion about this, the readers are referred to the previously published papers [19,37–40]. The <2 μm fractions of Mt clays collected from Hojun bentonite (Gunma, Japan) were successively (1) treated with dithionite-citrate [41] and 2% Na_2CO_3 [42] to remove Fe oxides and amorphous Al and Si oxide coatings; (2) then washed four times in 1 M CH_3COONa – 1 M NaCl (pH 5) to Na-saturate the exchange complex; (3) rinsed with 80% methanol until free of Cl^-; and (4) then with acetone. The Na-saturated Mt clays were then air-dried and gently ground in an agate mortar. For HyA ionic solution, 80 mL of 0.1 M $AlCl_3$ solution was titrated with 160 mL of 0.1 M NaOH at the rate of 0.2–0.5 mL min^{-1} with continuous stirring to give a NaOH/Al molar ratio of 2.0. The resultant 240 mL of HyA ionic solution was diluted to 2 L (final Al concentration ≈4 mM) and aged for 7 d at 293 K. The pHs of the solution was recorded and clear filtrates were obtained by passing through a 0.2 μm pore size cellulose–NO_3 membrane filter (Toyo-Roshi Co., Tokyo) to remove the solid particles of $Al(OH)_3$ (if any). The filtrate (final HyA ionic solution) was used to synthesize HyA–Mt complex. The Al concentration in the filtrate was determined according to Davenport [43]. The final HyA ionic solution had a pH of 4.15 and an Al concentration of 3.96 mM.

The HyA–Mt complex was obtained through repeated reaction between Na-saturated Mt and the HyA solution as described by Inoue and Satoh [44]. The complexes were then made Cl^- free through washing with 80% methanol, washed with acetone, air-dried, gently ground, and passed through a 0.246 mm sieve. The amounts of Al adsorbed on the Mt was estimated as the difference between that present in the solution initially and that remaining in the solution after reacting with the clay.

The synthesized HyA–Mt complex was characterized for its charge, surface, and other relevant characteristics following the recognized methods (see [19,37–40]). The negative charge characteristics of untreated Mt and HyA–Mt were evaluated based on their CECs determined at different pHs across the range of 4.0–7.5 following the method of Wada and Okamura [45] with only a minor modification [19,39–40]. The PZSE of the HyA–Mt was determined by a modified salt titration method [46]. The total and external surface areas of the clay samples were determined by ethylene glycol mono-ethyl ether (EGME) method [47] and by adsorption of N_2 gas at 78 K using a BET surface area analyzer (Shibata P-850, Shibata-Kagaku Co., Tokyo), respectively. The internal surface area was calculated as the difference between total and external surface areas. The X-ray diffraction (XRD) analysis of K- and Mg-saturated, parallel oriented clay specimens was carried out with a Rigaku X-ray diffractometer (RAD-1A) (Rigaku Co., Tokyo) using Fe-filtered Co Kα radiation generated at 30 kV and 10 mA. To further characterize the HyA–Mt, the K-saturated (and air-dried) specimens were heated at 383, 573, and 823 K and the Mg-saturated specimens were solvated with glycerol, and their X-ray diffractograms recorded after each treatment. The clay specimens were also examined by IR absorption spectroscopy. One milligram of sample was mixed with 200 mg of KBr, the mixtures were pressed to pellets, and the KBr pellets were then examined by a Fourier-transform infrared (FTIR) spectrometer (Bio-Rad, Cambridge, MA).

2.2. Adsorption–desorption experiments

All the adsorption–desorption experiments of this study were conducted in duplicate. The procedures for these experiments are described hereunder.

2.2.1. Adsorption isotherm

Before commencing the actual experiments aiming at investigating the surface coverage effects on the desorption kinetics of preadsorbed Se from the HyA–Mt complex, an adsorption isotherm