

# Adsorption studies of Mo and V onto ferrihydrite

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## ABSTRACT

In this paper, the kinetics of Mo and V (100  $\mu\text{M}$ ) uptake on ferrihydrite (FHY) were evaluated in batch, mono-sorbate systems at pH between 4 and 9, and in bi-sorbate systems in the presence of P (100  $\mu\text{M}$ ) at pH 7. In the Mo and V single-sorbate experiments, 100% adsorption was observed at pH values below 6 and 8, respectively. Above the point of zero charge (PZC = 7.97) of FHY, the adsorption efficiency for Mo dropped dramatically (20% at pH 8) while V showed high uptake efficiencies even at pH 9 (60% efficiency). The results from the bi-sorbate experiments (Mo-P and V-P) showed that at pH 7, P out-competed (97%) Mo for binding sites on FHY, while in the V-P binary system only ~44% of the binding sites are occupied by P with the remaining sites being occupied by V.

## Introduction

MOLYBDENUM (Mo) and vanadium (V) are important micronutrients for all living organisms and the lack or excess of these elements may lead to functional enzymatic disequilibria (Kisker *et al.* 1997; Mukherjee *et al.* 2004). Mo and V cycling in the environment are controlled by adsorption, ion exchange or complexation onto/with various bio- and geo-sorbents. Among the inorganic materials that can interact with Mo, V and phosphate (P) are poorly ordered Fe oxyhydroxides (e.g. ferrihydrite), which have a very high surface area and a high affinity to adsorb or incorporate and thus control the availability of different ions in terrestrial environments (Goldberg *et al.*, 2002; Metz and Trefry 1988; Trefry and Metz 1989). High affinities for molybdate (Gustafsson 2003), vanadate (Feely *et al.* 1998) and phosphate (Cornell and Schwertmann 2000; Gustafsson 2003; Michel *et al.* 2007) for Fe oxyhydroxides have previously been documented in the literature. However, little is known about the synergistic effects among these elements and their influence on uptake

efficiency. Our research focused on the effects of pH and P competition on Mo and V adsorption onto FHY as well as on the comparison between the Mo, V and P affinities for FHY surface sites. In addition, kinetic information about Mo and V adsorption as a function of pH were extracted and a mechanistic model for the adsorption processes is discussed.

## Methods and materials

Ferrihydrite was synthesized following the methods described by Cornell and Schwertmann (2000). The resulting material was characterized for its crystallinity (XRD, 2-line FHY), surface area (BET = 193  $\text{m}^2\text{g}^{-1}$ ), point of zero charge (potentiometric titrations, PZC = 7.96) and size (high-resolution transmission electron microscopy, 3–5 nm individual particles within large aggregates). Mono-sorbate batch-adsorption studies with 0.1  $\text{g L}^{-1}$  FHY (dried weight – DW) and 100  $\mu\text{M}$  Mo and V, respectively, were conducted under constant mixing at room temperature and under a  $\text{N}_2$  atmosphere. The FHY was used as fresh slurries and the materials were only dried to establish the DW needed for the kinetic calculations. Experiments were carried out for 1280 min with solution aliquots sampled at

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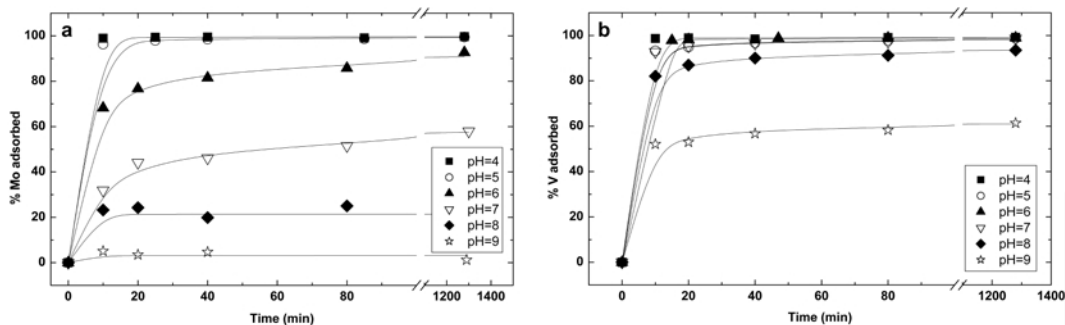


FIG. 1. Mo (A) and V (B) adsorption onto FHY ( $C_i = 100 \mu\text{M}$  metal and  $C_{\text{FHY}} = 0.1 \text{ g L}^{-1}$  FHY) at different pH values in the mono-sorbate systems. Symbols represent experimental data and lines show the fits to a pseudo-second order kinetic model. Errors in metal concentrations were smaller than the size of the symbols.

specific time steps via filtration ( $0.2 \mu\text{m}$ ) for Mo and V analyses by ICP-OES (detection limit of  $0.6 \mu\text{g L}^{-1}$  for Mo and  $0.9 \mu\text{g L}^{-1}$  for V). The effect of pH (between 4 and 9 in pH stat mode, and at ionic strength (IS) 0.01) and the competition for binding sites on the FHY surface with phosphate (bi-sorbate batch systems; pH 7, P analysed with spectrophotometric acid acetate–molybdenum blue method (Kuo 1996) were tested.

Metal-removal efficiencies were calculated using equation 1.

$$E = \frac{C_i - C_t}{C_i} \cdot 100 \quad (1)$$

where  $E$  is the removal/adsorption efficiency capacity (%),  $C_i$  is the initial metal concentration and  $C_t$  is the metal concentration (both in  $\text{mmol L}^{-1}$ ) at any time,  $t$ . The removal efficiencies were weighted and fitted to the pseudo-second order kinetic model described previously in the literature (Herrero *et al.*, 2006).

## Results and discussions

Figure 1 shows the Mo and V removal efficiencies vs. time at different pH values. Both Mo and V are removed faster at low pH (within 20 min for Mo and 10 min for V). However, FHY has a higher apparent affinity for V compared with Mo.

The adsorption efficiency for Mo was high at pH <6 (90–100%) but decreased with increasing pH (i.e. pH 7 <60%, pH 8 <20% and pH 9 <3%), while for V the adsorption efficiency decreased to ~60% only at pH 9. This pH-dependent behaviour (Fig. 2) reveals that below pH = 6, both V and Mo have the greatest affinity for the FHY binding

sites. Our results agree well with the FHY surface charge results (FHY protonated below pH 7.9, PZC) obtained by Trivedi *et al.* (2003) and also with the data of Gustafsson (2003) who studied Mo ( $50 \mu\text{M}$ ) adsorption onto FHY ( $1 \text{ g L}^{-1}$ ) at pH 3–8.

There have been no previous studies related to V sorption onto FHY in low ionic strength (i.e. fresh-water) systems published. However, Trefry and Metz (1989) cited an 80% V removal efficiency in seawater ( $200 \mu\text{M}$  V,  $2 \text{ g L}^{-1}$  FHY, pH 8, IS 0.7) while in the present study, at pH 8 the efficiency was still >90%, thus indicating the ionic-strength effect.

The experimental data obtained from the P competitive adsorption studies at pH 7 (Fig. 3) showed that in the mono-sorbate (P) and bi-sorbate studies (P-Mo and P-V), the P uptake achieved steady state within 80–100 min. However, as shown above, in the mono-sorbate Mo and V systems the adsorption process was

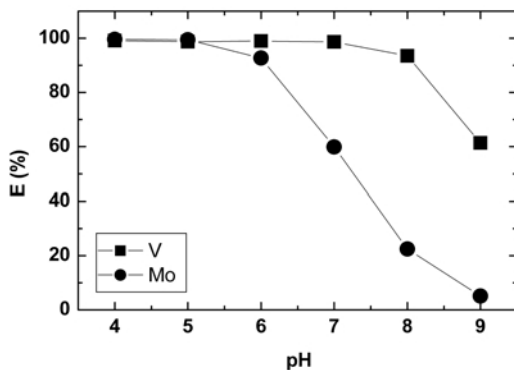


FIG. 2. The influence of pH on Mo and V removal efficiencies ( $E$ ) by FHY. ( $C_{\text{Mo/V}} \approx 100 \mu\text{M}$ ,  $C_{\text{FHY}} = 0.1 \text{ g L}^{-1}$ ).

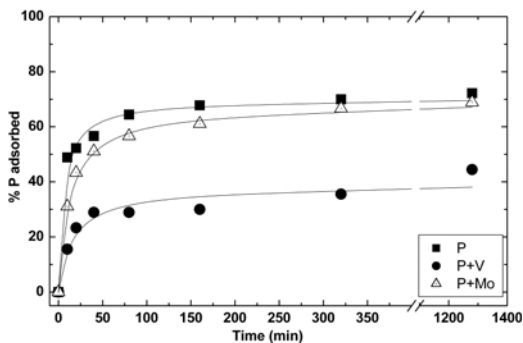


FIG. 3. Competitive adsorption between Mo, V and P ( $C_i = 100 \mu\text{M}$ ;  $C_{\text{FHY}} = 0.1 \text{ g L}^{-1}$ , pH 7).

significantly faster (within 10 min for V and 20 min for Mo). The weighted maximum uptake efficiency of P in the mono-sorbate system was 70%, while when equal concentrations of V and P (100  $\mu\text{M}$ ) were added to the system, the maximum P uptake efficiency decreased to ~40% suggesting that almost half of the available binding sites on the FHY were occupied by vanadate ions. In the presence of Mo, no significant effect on the P maximum uptake efficiency was observed (Fig. 3).

For comparison, Gustafsson (2003) showed that the presence of P (200  $\mu\text{M}$ ) in Mo-FHY sorption system (pH 7; 50  $\mu\text{M}$  Mo; 0.1 g FHY  $\text{L}^{-1}$ ) reduced the Mo adsorption efficiency from 80% to 8%. His study revealed that at pH = 7 and a P:Mo ratio of 4:1, P out-competes Mo (~8% Mo and 92% P). In the present study conducted at a lower P:Mo ratio of 1:1, P still out-competes Mo (<3% Mo and 97% P).

## Conclusion

Our results confirm previous findings regarding the pH dependency of anion adsorption to poorly ordered, high surface area Fe nanophases (Cornell and Schwertmann, 2003; Dzombak and Morel, 1990; Gustafsson, 2003). Both Mo and V anions are adsorbed quickly (within 20 min) but V had a greater absorption affinity over a larger pH interval when compared with Mo. The adsorption trends and kinetics are well explained by the FHY surface-charge properties. Above the FHY PZC (i.e. > pH = 8) the decrease in Mo and V uptake can be correlated with the change in uptake mechanism due to the change in apparent surface charge of FHY. The sorption reactions could be fitted with a pseudo-second order kinetic model

with the mechanism probably being chemo-adsorption (Herrero *et al.*, 2006). In contrast, above the PZC (greater competition between  $\text{OH}^-$  and aqueous Mo and V anions for available surface sites), the adsorption is limited by the weak binding forces. The results obtained from the P competitive adsorption studies showed that P (55%) and V (45%) competed almost equally for the FHY binding sites, whereas in the P-Mo bi-sorbate system, P was preferentially adsorbed (97%).

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