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Adsorption of vanadium(V) polymers on ferrihydrite and hematite

Colton J. Vessey[a], Michael P. Schmidt[c], Mojtaba Abdolahnezhad[b], Derek Peak[c], Matthew B.J. Lindsay[b]*

[a]Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, AB, T6G 2E3, Canada
[b]Department of Geological Sciences, University of Saskatchewan, Saskatoon, SK, S7N 5E2, Canada
[c]Department of Soil Scinces, University of Saskatchewan, Saskatoon, SK, S7N 2V3
(*correspondence: matt.lindsay@usask.ca)

Vanadium (V) is widely used in industrial processes (e.g., catalysis), manufacturing (e.g., steel making), and as a proxy for studying biogeochemical processes over geologic time [1]. However, anthroprogenic releases of this potentially hazardous transition metal have increased in recent decades [2]. While several studies have observed uptake of mononuclear V species (i.e., $H_xVO_4{}^{(3-x)-}{}_{(aq)}$) by iron (oxyhydr)oxides [3], reactions involving polynuclear species ($[H_xV_2O_7]^{(4-x)-}$, $V_4O_{12}{}^{4-}$, and $[H_xV_{10}O_{28}]^{(6-x)-}$) have not yet been characterized. We examine surface comlextion of (poly)vanadate species on ferrihydrite [$5Fe_2O_3{\cdot}9H_2O$] and hematite [α-Fe_2O_3] using *in situ* attenuated total reflectance – Fourier transform infrared spectroscopy (ATR-FTIR).

We collected the ATR-FTIR spectra on an Invenio-R FTIR spectrometer using a Bruker Platinum ATR with a single-bounce ZnSe/diamond internal reflective element (IRE) with a 45° incidence angle. Ferrihydrite and hematite were drop cast (10 g L^{-1}) onto the IRE and equilibrated with 0.05 M NaCl background electrolyte. Adsorption isotherms were then produced by equilibrating V(V) solutions (50, 100, 250, 500, 750, 1000, 3000 and 5000 μM) with ferrihydrite or hematite films under constant flow at pH 3, 4, 5, and 6.

Our results reveal pH- and concentration-dependent adsorption of mononuclear and polynuclear V species at both ferrihydrite and hematite surfaces. Adsorbed polynuclear species were prevalent at $[V]_T > 250$ μM. Ferrihdyrite had a limited capacity to adsorb polyvanadate species at pH 5 and 6, whereas surface polymers were evident at all experimental pH values during adorption onto hematite. Our findings indicate the importance in considering the sequestration and fate of V(V) polynuclear species in the environment.

[1] Huang et al. (2016) *Chem. Geol.*, **417**, 68–89. [2] Watt et al. (2018) *Environ. Sci. Technol.*, **52**, 11973–11974. [3] Brinza et al. (2015) *Cryst. Growth Des.*, **15**, 4768-4780.