

5 Residence Time Effects of Arsenate Adsorption/Desorption Mechanism at the Aluminum Oxide-Water Interface

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Soils and sediments are nearly always at disequilibrium with respect to ion transformations, therefore the rate of contaminant (metal/metalloid) bioavailability can be reduced or increased over time. In this study, we investigated the residence time effects (1day-11months) on As(V) adsorption/desorption mechanisms at the aluminum oxide-water interface using a combination of batch adsorption (pH 4 and 8, 5 g L^{-1} , $[\text{As(V)}]_0=1\text{mM}$, $I=0.1\text{M NaNO}_3$) and desorption experiments and Extended X-ray Absorption Fine Structure spectroscopy (EXAFS). The As(V) adsorption kinetics at both pHs show an initial fast reaction (<4h) followed by slow continuous adsorption over 24h. The As(V) adsorption increases with decreasing pH, resulting 87% of the total adsorption after 24h at pH 4 and whereas only 40% of the total absorption occurred at pH 8. The EXAFS data indicate that As(V) predominantly formed inner-sphere bidentate binuclear complexes between 1day and 1month at constant loading levels ($\cong 0.18\text{mM g}^{-1}$ at pH 4 and $\cong 0.10\text{mM g}^{-1}$ at pH 8), as evidenced by a As(V)-Al bond distance of $\cong 3.11\text{ \AA}$. The As(V) adsorption mechanisms were further investigated at aging times up to 11months. The stability of aged samples was also investigated using the batch desorption experiments, replenishing with buffered background electrolyte every 24h for 25days.