

Predicting Reactivity at the Aqueous-Mineral Interface: A Computational Approach to Contaminant Adsorption

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Understanding the aqueous interactions between inorganic/organic species and mineral surfaces is crucial for predicting environmental processes and assessing the fate of contaminants. Hematite ($\alpha\text{-Fe}_2\text{O}_3$) and alumina ($\alpha\text{-Al}_2\text{O}_3$) are isostructural metal oxide minerals with known ability to bind contaminants including heavy metals (Pb), oxyanions (AsO_4^{3-} , PO_4^{3-} , SO_4^{2-}) [1], and organic acids and polyphenols [2]. By combining Density Functional Theory (DFT) calculations, thermochemical data, and tunable experimental parameters (pH, temperature, concentration), we developed thermodynamic cycles to compute adsorption energetics and predict aqueous surface reactivity. This approach accurately differentiates between inner- and outer-sphere adsorption preferences and reflects experimentally derived reactivity trends based on surface composition and facet. We provide a fundamental understanding of how these species bind to unique sites on mineral surfaces, elucidating factors that govern adsorption on different crystal facets such as strain, surface topography, and surface functional group identity. Working closely with experimentalists, we make connections to spectroscopic measurements, providing a means for interpreting complex spectra and assigning binding modes. By deciphering the underlying mechanisms driving contaminant sorption at the molecular-level, we provide new insights into the reactivity of naturally-occurring phases as a function of structure and composition, expanding geochemical understanding while forming a basis for future material science efforts aimed at rational sorbent design.

[1] Tamijani, et al. (2020), *Langmuir*, 44, 13166-13180.

[2] Augustine, et al. (2022), *J. Coll. Inter. Sci.*, 609, 469-481.

