

Schwertmannite as a new sorbent for phosphate immobilization: The role of pH and sulfate release

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Schwertmannite is a nanocrystalline ferric oxyhydroxysulfate mineral with a variable chemical composition, simplified as $\text{Fe}_8\text{O}_8(\text{OH})_{8-2x}(\text{SO}_4)_x$ (with $1 \leq x \leq 1.75$). Although there is still some controversy with regard to its actual structure, schwertmannite is typically described as an akaganeite-like framework of iron(III) octahedra with a tunnel structure that hosts inner- and outer-spherical complexes of sulfate. Due to its high specific surface area and the ability to incorporate oxyanions into the tunnel cavities, schwertmannite has recently been proposed as a promising sorbent for environmental remediation technologies to immobilize phosphate. Phosphate sorption to schwertmannite is likely to occur via ligand exchange with surface and tunnel sulfate, resulting in the release of sulfate. The importance of phosphate interaction with sulfate groups and its consequences for the structure of schwertmannite are still poorly understood, hampering the use of schwertmannite as a sorbent in natural systems.

Here, we investigated phosphate sorption, concomitant sulfate release and their impact on the structure of schwertmannite as a function of pH and phosphate loading. Kinetic and equilibrium batch experiments with synthetic schwertmannite were performed at pH 3, 6, and 8, and solid-phase samples of unreacted and phosphate-sorbed schwertmannite were analyzed using a combination of diffractometric, spectroscopic, and microscopic techniques.

Phosphate sorption to schwertmannite resulted in the substitution of up to ~90% of all solid-phase sulfate. Alkaline conditions were more favorable for phosphate sorption despite an increase in electrostatic repulsion, which we attributed to sulfate groups being more loosely (outer-spherically) bound at higher pH. Diffractometric and scanning electron microscopic analyses suggest no transformation to other mineral phases and no morphological changes during equilibration with phosphate. However, infrared spectra showed a broadening of the sulfate vibrational bands with increasing pH, confirming a change in sulfate speciation with pH. ⁵⁷Mössbauer showed that the solid-phase did not undergo major mineralogical changes, but in the presence of phosphate, the proportion of partially ordered schwertmannite decreased, indicating a loss in crystallinity.

Our results are important for a fundamental understanding of the sorption properties of schwertmannite in phosphate-rich environments as they point towards the central role of sulfate coordination for phosphate immobilization by schwertmannite.