

## Size distribution of ferrihydrite aggregate and its effects on metal adsorption and transport

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Ferrihydrite, iron oxyhydroxide nanomineral (< ~ 100 nm in size), is ubiquitous on the surface of the Earth. Ferrihydrite has a large capacity to adsorb heavy metals in solutions because of its large specific surface area. The adsorbed metals onto ferrihydrite are transported in ground and river waters, affecting the redistribution of the metals in surface environments. Ferrihydrite forms aggregates with various sizes and this can affect the uptake behavior of heavy metals and the subsequent transport. Furthermore, filtration with 450- or 220-nm pore, which is the most frequently used to physically separate ferrihydrite in adsorption measurements, can give incorrect concentrations of adsorbates because of the extremely small size of ferrihydrite primary particles.

For the present study, ferrihydrite was investigated by various methods to understand the size distribution and the influence of metal adsorption on the size distribution, and then a possible impact on the transport of adsorbed metals was discussed. Size distribution of ferrihydrite and its aggregates were examined by gravitational settling, centrifugation, dynamic light scattering and transmission electron microscopy (TEM). Adsorption experiments of Zn at acidic to neutral pH were performed with ferrihydrite of various concentrations.

Direct observation by TEM revealed that individual, spherical ferrihydrite nanomineral of ~ 5 nm was indeed present, but they formed aggregates of around 100 nm. Meanwhile, the other methods for size distribution indicated that suspended ferrihydrite in solution formed aggregates of several tens of nm to a few tens of microns. The size distribution varied with pH and Fe concentration; smaller aggregates were formed at lower pH and lower Fe concentration. Despite the size distribution, most aggregates did not pass through filters with 450-nm pore.

The amounts of Zn adsorbed on ferrihydrite were measured for solutions with aggregates fractionated by size, and then, they were calculated on the assumption that the adsorption occurred on the surface of individual 5-nm ferrihydrite nanominerals. Good agreement between the measured and calculated amounts of Zn suggests that the structures of the aggregates are loose enough for Zn ions to diffuse into the aggregates and reach to individual nanominerals. It turned out that conventional adsorption experiments with relatively high Fe concentrations could describe metal adsorption almost correctly.

Sedimentation of particles depends on the size, in general; it takes about ten days for ferrihydrite aggregates of 100 nm in diameter to settle down on the bottom of solution of 10 mm height. This implies that heavy metals adsorbed on the aggregates with 100 nm or larger sizes are not transported further in water systems, whereas those on smaller aggregates are transported further.

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