In situ Observations of Struvite Crystallization: Relevance for Phosphorus Recovery from Wastewaters

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Concerns about an impending scarcity of natural rock phosphate resources have led to the exploration of new phosphorus (P) extraction methods from alternative sources. One prime P recovery method is from municipal and industrial wastewaters by the controlled crystallization of struvite ($MgNH_4PO_4 \cdot 6H_2O$). This is highly attractive, because struvite can directly substitute conventional fertilizers and be used as a slow-release fertilizer, thus helping to reduce the demand on rock phosphate and the environmental impact of excess P release into aquatic systems.

Struvite crystallization has so far been studied mostly via indirect, *ex-situ* imaging and bulk diffraction of quench-dried samples, all methods that are known to suffer from various problems. A mechanistic understanding of the struvite crystallization pathways is still lacking, although the efficiency of struvite-based P recovery processes critically depends on such knowledge. To fill this knowledge gap we used liquid cell atomic force microscopy and synchrotron-based X-ray scattering to directly follow in an *in situ* and time-resolved manner the heterogeneous and homogeneous nucleation and crystallization of struvite from aqueous media. Our results indicate that both the heterogeneous and homogeneous formation of struvite occur through a particle-mediated process that involves the fast precipitation of apparently non-crystalline nanoparticles (~50 nm in size) that later self-assemble and transform into crystalline struvite.

Our work is the first to report such a two-step process for struvite crystallization. This new knowledge contributes to the discussion regarding the early stages of crystal formation in general and may provide a key in designing novel struvite-based fertilizers.