



Phosphorus and nitrogen recovery in crystalline struvite formed from magnesium mineral sources

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Nutrient removal from wastewater is a great challenge to avoid eutrophication of water bodies (i.e. rivers, lakes). Simultaneously nutrient recovery is of high importance since mineral resources, especially natural phosphorus sources are becoming increasingly limited. Towards the sustainable development of nutrient resources, phosphorus and nitrogen removal and recovery from municipal and/ or industrial wastewater treatment plants, in the form of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) is considered an attractive alternative for both water remediation as well as the use of wastes into a slow-release fertilizer in agriculture (Kofina & Koutsoukos, 2005; Mpountas et al., 2017). In this study among different Mg sources, low cost magnesia, MgO and the natural Mg-rich brucite mineral, $\text{Mg}(\text{OH})_2$ were used for macroscale and nanoscale struvite precipitation experiments, respectively. During hydration or upon contact with water magnesia converts to a small or to a large degree, depending on the solution conditions, into brucite. Thus the role of brucite as a substrate for struvite overgrowth was investigated. The metastable zone width of solutions supersaturated with respect to struvite at constant pH, 25 °C was determined. The kinetics of both spontaneous and seeded growth of struvite in supersaturated solutions was investigated in batch reactors (of working volume 1 L) at constant solution supersaturation. Continuous addition of titrant solutions of MgCl_2 or MgO saturated solution, $\text{NH}_4\text{H}_2\text{PO}_4$ and NaOH (pH readjustment of working solution) according to ionic mass balance calculations, maintained solution supersaturation constant during batch growth experiments. Struvite spontaneous precipitation and struvite seed-growth experiments from $\text{MgCl}_2/\text{NH}_4\text{H}_2\text{PO}_4$ supersaturated solutions at pH 9 followed a surface diffusion-controlled mechanism. Both growth experiments from saturated magnesia solutions supersaturated with respect to struvite at pH 9.9 were dominated by crystal growth rather than nucleation (primary or secondary). At relatively high solution supersaturation with respect to struvite and pH ca. 9.9 in magnesia saturated solutions, the inoculation of magnesia powder seeds resulted in the precipitation of $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$. Saturated magnesia solutions were shown to be an effective alternative magnesium source for phosphorus recovery from ammonia and phosphorous rich solutions through struvite precipitation. In situ AFM experiments using freshly cleaved brucite, $\text{Mg}(\text{OH})_2$, surfaces were performed at flow conditions with ammonium-phosphate-rich solutions. The precipitation of struvite crystals was observed along brucite step-edges, where dissolution and hence release of Mg was greater. AFM observations corroborated conclusions drawn from bulk crystal growth experiments.

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References: Kofina & Koutsoukos (2005) *Cryst. Growth Des.* 5, 489–496; Mpountas et al. (2017) *J. Chem. Technol. Biotechnol.* 92, 2075–2082.