

Phosphorus and nitrogen recovery from wastewater in the form of struvite: alternative magnesium sources

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Abstract

Recovery of phosphorus and nitrogen from municipal and other types of wastewater may be achieved through the direct crystallization of struvite (magnesium ammonium phosphate hexahydrate, $\text{Mg}\cdot\text{NH}_4\cdot\text{PO}_4\cdot 6\text{H}_2\text{O}$). Wastewater deficiency in magnesium makes it necessary for the external addition of magnesium to make up for the supersaturation needed. In the present work we have tested artificial seawater and saturated with respect to calcined magnesia (MgO) aqueous solutions as magnesium sources, as both sources are low cost and readily available. Both the spontaneous precipitation and the seeded crystal growth have been investigated at constant supersaturation (pH 9.0- 10.0, 25°C). Seawater accelerated the precipitation of struvite and narrowed the stability domain of the supersaturated solutions. Saturated magnesia solutions were shown to broaden the stability domain of the struvite supersaturated solutions. Magnesia suspensions were also tested with respect to their ability to induce crystallization of struvite. Measurement of the kinetics of crystal growth by potentiometric methods maintaining solution supersaturation, and AFM observations showed that the solid particles in magnesia saturated suspensions, provide favorable substrate for the overgrowth of struvite in combination with the appropriate supersaturation conditions.

Keywords: struvite, precipitation of, artificial seawater, magnesia, crystal growth

1. Introduction

High phosphorus and ammonia accumulation in anthropogenic waste streams results into environmental problems such as eutrophication. A promising solution towards phosphorus and ammonia recovery is considered the low-soluble struvite (magnesium ammonium phosphate or MAP, $\text{MgNH}_4\text{PO}_4\cdot 6\text{H}_2\text{O}$) precipitation. Because wastewater effluents are poor in Mg content, additional Mg sources are needed including soluble magnesium salts (chlorides and/or nitrates (Kofina et al., 2005; Mpountas et al., 2017) while Mg-rich seawater and MgO may be considered as low cost alternatives. In the

present work the use of different magnesium sources i.e. artificial seawater, magnesia, brucite for struvite precipitation was tested through measurements of the kinetics of struvite formation in aqueous media at conditions simulating the composition of domestic wastewater in terms of nitrogen, phosphorus concentration levels and salinity. *in situ* AFM measurements were done on freshly cleaved brucite, $\text{Mg}(\text{OH})_2$ to investigate the ability of this substrate for struvite overgrowth.

2. Experimental

2.1. precipitation experiments

The investigation was carried out in aqueous solutions with compositions typically encountered in seawater (Kester, 1967). For struvite crystallization experiments in the presence of Mg-source of magnesia, magnesia saturated solution was prepared after suspension of magnesia solids in NaCl 0.1 M. The experimental procedure and the experimental set-up are described elsewhere in details (Kofina et al., 2005).

2.2 Nanoscale experiments

In situ, real time imaging AFM (Bruker Multimode Atomic Force Microscope operating in contact mode) in connection with a fluid reaction cell was used. For the in-situ AFM experiments natural freshly cleaved optically transparent brucite crystals from the Tallgruvan (Norberg, Sweden) were obtained. The final dimensions of the brucite specimens used in the AFM experiments were ca. 3x3x0.2 mm.

3. Results and Discussion

The stability domain of struvite in artificial seawater and report on the kinetics of spontaneous struvite precipitation are presented in Fig. 1a. Struvite precipitation from the supersaturated solutions ($1 \leq \Omega \leq 2.8$) prepared in MgCl_2 was initiated spontaneously past the lapse of defined induction times (Fig. 1a). The

measurements of the induction times showed that the stability range of the supersaturated solutions in artificial seawater was very narrow ($1 \leq \Omega \leq 1.5$). The rates of the struvite precipitating past the end of the induction period were measured at a constant driving force by the addition of stoichiometric titrant solutions throughout the precipitation process, using solution pH as a master variable monitored by a glass electrode sensor.

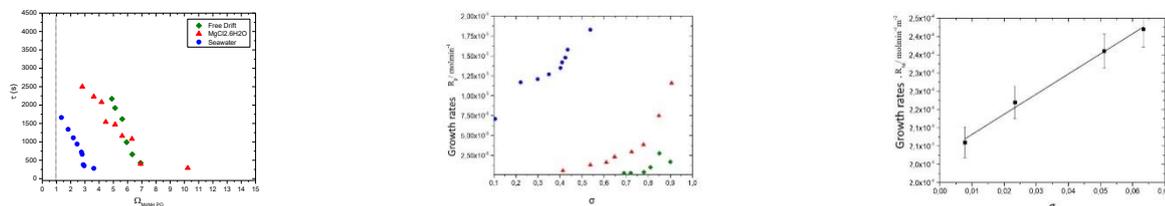


Figure 1. (a) Stability diagram for struvite; (b) Plot of the rates of struvite precipitation as a function of the solution supersaturation, 25 °C from Mg-sources of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (free drift) (\blacklozenge) and at constant supersaturation and constant solution pH 9 with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (\blacktriangle) and seawater (\bullet); (c) Plot of the rates as a function of relative supersaturation after inoculation of 100 mg struvite seeds ($\text{BET} = 0.47 \text{ m}^2 \cdot \text{g}^{-1}$), with Mg-source of seawater at constant supersaturation, 25°C, pH 9.0.

Similar diagrams were obtained using saturated magnesia solutions in water for the preparation of the supersaturated solutions. In Figure 2, AFM deflection images showing struvite precipitation with elongated prismatic nanoparticle(s) on a brucite crystal surface during reaction with 500 mM $(\text{NH}_4)_2\text{HPO}_4$ (pH 8.5 past

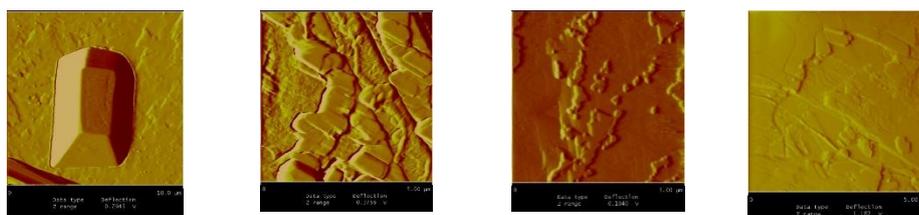


Fig. 2. AFM deflection images showing struvite crystals shaped nanoparticles nucleated on a brucite surface during reaction with solutions of (a), (b) $(\text{NH}_4)_2\text{HPO}_4$ 500mM pH 8.5. The differences in brucite morphology in contact with solutions of $\text{NH}_4\text{H}_2\text{PO}_4$ (c) 100 mM and (d) 500 mM did not reveal struvite precipitation that was confirmed by Raman analysis.

4. Conclusions

It is possible to use seawater as a magnesium source to recover P from the respective supersaturated solutions. Seawater matrix reduced the stability domain of the struvite system and accelerated the rates of struvite formation, homogeneous or heterogeneous. Saturated magnesia may be used as magnesium source to recover

The rates of precipitation measured from the titrants addition showed a linear dependence on the solution supersaturation (Fig. 1b) suggesting surface diffusion-controlled mechanism. The dependence of the rates of crystal growth, of struvite seed crystals on the solution relative supersaturation was linear, suggesting surface diffusion-controlled mechanism (BCF) (Fig. 1c).

overnight equilibration with the mother liquid. Growth of particles was observed at different scanned areas along the step edges (Fig. 2a,b). AFM deflection images showed larger particle aggregates formed and the formation of struvite was confirmed by SEM and Raman spectroscopy.

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struvite, even though the precipitation rates were lower in comparison with the rates obtained in solutions in which magnesium chloride was used as magnesium source. Epitaxial growth of struvite on brucite is suggested by AFM measurements.

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