

STRUVITE PRECIPITATION FROM Mg-RICH AQUEOUS SOLUTION: MACRO- TO NANOSCALE EXPERIMENTS

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ABSTRACT

The aim of this study was the investigation struvite precipitation from supersaturated solutions using different magnesium sources. Macro- to nanoscale experiments were performed in artificial seawater and calcined magnesite saturated solutions, supersaturated with respect to struvite. The stability domain and the kinetics of both spontaneous and seeded growth of struvite in supersaturated solutions were measured at constant solution supersaturation with respect to struvite. Solution supersaturation was maintained by the addition of titrant solutions according to the stoichiometry of the precipitating salt. Artificial seawater and saturated magnesite solutions were both promising alternatives for phosphorus recovery from ammonia and phosphorous containing solutions through struvite precipitation. In situ AFM observations of struvite heterogeneous nucleation and crystal growth on freshly cleaved brucite, $Mg(OH)_2$ revealed the possibility of brucite implication towards struvite recovery from wastewater effluents. The solids were characterized by XRD, SEM and Raman spectrometry.

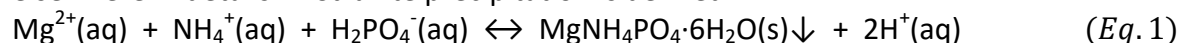
INTRODUCTION

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, $MgNH_4PO_4 \cdot 6H_2O$) precipitation. Struvite could be used as slow-release fertilizer in agriculture. Due to the lack of Mg^{2+} in wastewater effluents supplements of Mg^{2+} are necessary for the simultaneous recovery of total ammonia-nitrogen, TAN and PO_4-P by struvite precipitation. Different Mg sources are needed including soluble magnesium salts (chlorides and/or nitrates^[1, 2] while Mg-rich seawater^[3] and MgO ^[4] may considered as low cost alternatives Phosphorus accumulation in several ecosystems is a consequence of phosphorus containing discharges from wastewater treatment plants (WWTPs) and/ or from the use of phosphorus in agricultural activities. Elevated phosphorus concentration levels in wastewater results in degradation of the water quality and in the formation of insoluble scale on the equipment and machinery used in wastewater treatment processes. Phosphorus concentration levels as low as ca. $\sim 0.02 \text{ mg} \cdot \text{L}^{-1}$ is considered responsible for eutrophication of natural aquatic systems. In eutrophic waters algal growth promotion may cause hypoxia and negative effects from algal toxins detrimental to aquatic biology^[5]. Additionally, phosphorus loading of wastewater streams may increase seasonally from the runoff from intensively fertilized soils or from industrial processes in which phosphate

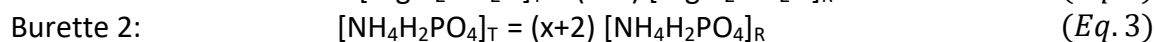
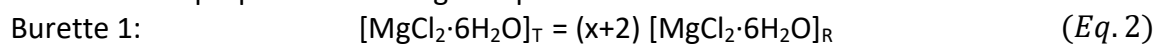
discharges are relatively high (i.e. dairies, food processing plants, metal finishing facilities, etc. ^[2]). Several scientific papers review the formation, control and recovery of crystalline MAP from primarily municipal wastewater and other waste streams ^[6-9]. Struvite precipitation, is a promising alternative for phosphorus recovery from effluents rich in ammonia and phosphorus ^[10]. Phosphorus recovery by struvite precipitation leads to environmental protection and is also contributing to sustainable development through raw material savings. Municipal wastewater usually contain high levels of phosphorus and nitrogen concentrations. However, they are poor in magnesium levels. The problem of magnesium source is very important from the point of view of application at WWTP, because usually wastewaters contain relatively low concentrations of magnesium. Abundant magnesia resources are found in Northern Greece. Brucite, Mg(OH)₂ on the other hand, although promising is less soluble than magnesia (MgO) and should therefore be considered rather as a template for the formation of struvite. Direct observations of the crystal growth process at the nano- level is possible through the use of Atomic Force Microscopy (AFM). A considerable number of studies have investigated the calcite growth by in-situ AFM imaging in a fluid-cell ^[11-14]. Hövelmann & Putnis ^[15] investigated the interactions of ammonium phosphate solutions with brucite cleavage surfaces by AFM suggesting coupled brucite dissolution and struvite precipitation at the mineral-fluid interface. The aim of this study was the investigation of different magnesium sources i.e. artificial seawater, magnesia, brucite for struvite precipitation. The kinetics of precipitation of struvite from its supersaturated aqueous solutions was investigated at conditions simulating the composition of domestic wastewater in terms of nitrogen, phosphorus concentration levels and salinity. Additionally in situ AFM experiments were performed using freshly cleaved brucite, Mg(OH)₂ in aqueous solutions at flow conditions to investigate possible struvite precipitation. Batch experiments were complemented to AFM experiments.

EXPERIMENTAL SECTION

MACROSCALE EXPERIMENTS. All experiments were carried out at 25 °C in a double-walled Pyrex vessel (250 mL and 1-L mL for crystallization experiments from Mg-source of artificial seawater and magnesia, respectively) thermostated by water circulation through a constant-temperature bath. Stock solutions of magnesium chloride hexahydrate and dihydrogen ammonium phosphate were prepared from corresponding crystalline solids MgCl₂·6H₂O and NH₄H₂PO₄ (Merck, reagent-grade) using triply distilled water. pH solution was adjusted to 9.0, by the addition of the appropriate amount of a standard solution of NaOH 1 M, followed by the addition of the appropriate volume of stock magnesium-rich solution. The investigation was carried out in aqueous solutions with compositions typically encountered in seawater ^[16]. 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 ^[1]. Struvite precipitation is defined:



In the struvite crystallization experiments carried out in struvite supersaturated solutions, in which the stoichiometric ratio of total magnesium (Mg_T):total phosphorus (P_T):total nitrogen (N_T) varied between 1:1:1 to about 1:4:4, depending on the magnesium source. The titrant solutions were prepared according to Eq. 2-4:



The spontaneous precipitation of struvite results to the decrease of pH solution thus the addition of NaOH 1 M was to maintain constant pH (pH 9.0) and was added in burette 2

$$[\text{NaOH}]_T = 2[\text{NaOH}]_R + (2 \cdot x)[\text{MgCl}_2 \cdot 6\text{H}_2\text{O}]_R \quad (\text{Eq. 4})$$

Labels of R and T represent solution concentration in the reactor and burettes, respectively; x factor equals to 21 and was derived after preliminary struvite precipitation experiments.

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.

RESULTS AND DISCUSSION

Seawater as magnesium source. 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. The rates of precipitation measured from the titrants addition showed a linear dependence on the solution supersaturation (**Fig. 1b**). The dependence of the rates on the solution supersaturation suggested a surface diffusion-controlled mechanism. XRD analysis (not shown here) confirmed struvite precipitation in all experiments. Since in spontaneous precipitation both nucleation and crystal growth take place, seeded crystal growth experiments were done in the stable domain of the supersaturated synthetic seawater solutions with respect to struvite. Crystal growth took place without the mediation of induction times. The dependence of the rates of crystal growth on the solution relative supersaturation was linear, suggesting surface diffusion-controlled mechanism (BCF) (**Fig. 1c**). This assumption was corroborated from the finding that the crystal growth rates were independent of the amount of crystal seeds inoculating the supersaturated solutions. Crystal growth apparently occurred on the active crystal growth sites and secondary nucleation never took place.

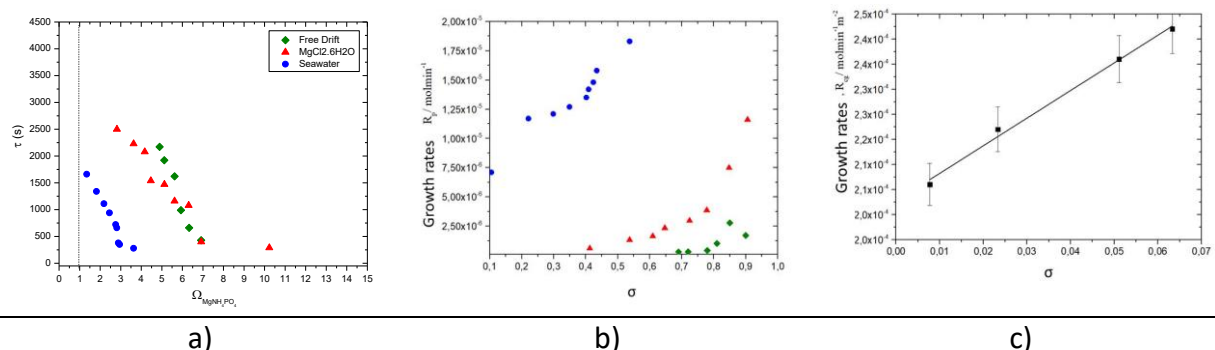


Fig. 1. a) Stability diagram for struvite; b) Plot of the rates of struvite precipitation as a function of the solution supersaturation, 25 °C from Mg-sources of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (free drift) (◆) and at constant supersaturation and constant solution pH 9 with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (▲) and seawater (●); 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.

MgO as magnesium source. Investigation of the spontaneous precipitation of struvite at constant pH, supersaturation and temperature yielded reliable kinetics measurements, since the driving force was maintained throughout the precipitation process. The profiles from which kinetics parameters are determined are often affected from the respective de-supersaturation profile compared to free drift experiments (**Fig. 2a**). Solution supersaturation was maintained through the continuous addition of reagents (MgCl_2 , $\text{NH}_4\text{H}_2\text{PO}_4$ and NaOH) at the appropriate concentrations, based on the stoichiometry of the precipitating solid ($\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-} = 1:1:1$) aiming at the replacement of the components removed from the solution to the precipitate. The width of the stable zone of the supersaturated solutions was found to correspond to supersaturation ratio values $1 < \Omega < 3.08$. In the case of MgCl_2 in supersaturated solutions in which $\text{Mg}_T:\text{N}_T:\text{P}_T$ was 1:1:1, and pH 9.0 the dependence of precipitation rates on supersaturation that suggested that struvite precipitation proceeds by a surface diffusion-controlled mechanism and the kinetics data were fitted to the polynuclear model for crystal growth. When magnesia was used as magnesium source at 25 °C, pH=9.90 \pm 0.05, and stoichiometric ratio $\text{Mg}_T:\text{N}_T:\text{P}_T$ in the range between 1:3:3 to 1:4:4. The stability limits were significantly broader than in the case of supersaturated solutions prepared with magnesium chloride. Moreover, the dependence of precipitation rates on supersaturation revealed that precipitation kinetics data obtained from supersaturated solutions prepared using saturated magnesia as magnesium source, gave a satisfactory fit to the spiral growth mechanism (Burton, Cabrera, Frank, BCF) model (**Fig. 2b**). It should be noted that the spontaneous precipitation process involves both nucleation and crystal growth of struvite, at least at the initial stages of the process. Crystal growth of struvite was investigated in stable supersaturated solutions, seeded with well characterized and aged struvite crystals ($\text{BET} = 0.47 \text{ m}^2 \cdot \text{g}^{-1}$). The supersaturated solutions were prepared with both magnesium chloride and magnesia. For magnesium chloride, at constant temperature of 25 °C, pH= 9.0 and a stoichiometric ratio of $\text{Mg}_T:\text{N}_T:\text{P}_T = 1:1:1$, a high order $n=3$ dependence of the crystal growth rates on the solution supersaturation was found, suggesting surface diffusion controlled mechanism. The kinetics data gave a satisfactory fit to the polynuclear model (**Fig. 2c**). For magnesia saturated solution supersaturated with respect to struvite, at 25 °C, pH= 9.9 \pm 0.05 and for values of the $\text{Mg}_T:\text{N}_T:\text{P}_T$ ratio between 1:1.16:1.16 to 1:1.4:1.4, the crystal growth rates dependence on the relative supersaturation gave a satisfactory fit to the spiral growth (BCF) model, as it was the case in spontaneous precipitation.

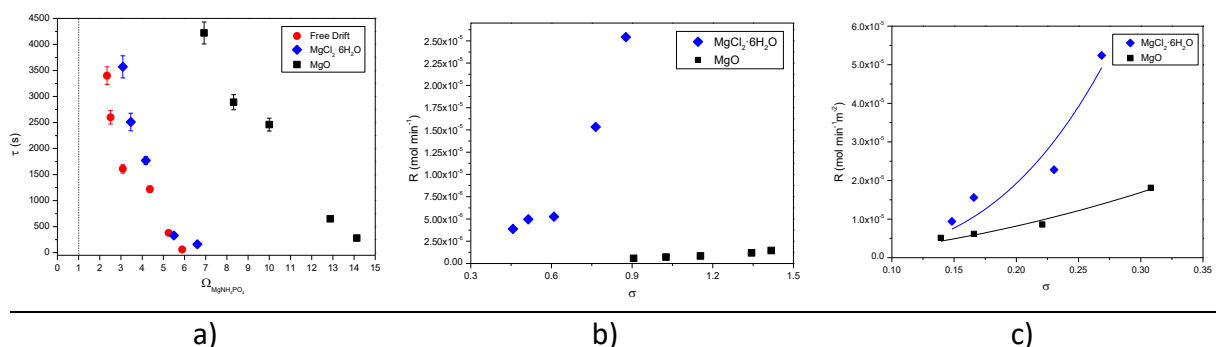


Fig. 2. a) Stability diagram for struvite; b) Plot of the rates of struvite precipitation as a function of the solution supersaturation, 25 °C from $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (free drift) (●), and constant supersaturation and pH 9 (◆); MgO , pH 9.9 (■); c) Plot of the rates as a function of relative supersaturation after inoculation of 100 mg struvite seeds, at constant supersaturation, 25 °C, with Mg-source of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, pH 9 (◆) and MgO , pH 9.9 (■).

For seeded growth experiments in the presence of magnesia seeds ($BET = 18.72 \text{ m}^2 \cdot \text{g}^{-1}$), supersaturated solutions with respect to struvite were prepared from MgO saturated solutions as magnesium ions source and $\text{NH}_4\text{H}_2\text{PO}_4$ at constant supersaturation and temperature of 25°C . The addition of a pre-weighed amount of crystalline magnesia (c.a. 25 mg) to the supersaturated solutions was done past equilibration for one hour, in order to confirm the stability of the respective solutions. According to the stability diagram (**Fig. 3a**), supersaturated solutions from MgO source were found to be stable for supersaturation values of $1 < \Omega < 6.92$. Consequently, these experiments were done within the stable supersaturated solutions domain. Seeding stable struvite supersaturated solutions prepared from saturated magnesia solutions, with magnesia powder particles yielded the formation of magnesium phosphate ($\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$, cattite) according to XRD analysis of the precipitate (not shown here).

Struvite nucleation and growth onto brucite (001) cleavage surfaces. **Fig. 3a** presents AFM deflection images showing struvite precipitation with elongated shaped particle(s) (with a size of $7 \times 4 \mu\text{m}$) on a brucite surface during reaction with 500 mM $(\text{NH}_4)_2\text{HPO}_4$ (pH 8.5) past overnight equilibration with the mother liquid. Growth of particles was observed at different scanned areas along the step edges (**Fig. 3a, b**). AFM deflection images showed larger particle aggregates formed and the formation of struvite was confirmed by SEM and Raman spectroscopy (**Fig. 4a-c, d**). AFM deflection images of brucite surface over a range of $\text{NH}_4\text{H}_2\text{PO}_4$ concentrations (100 and 500 mM, pH 8.5) overnight enhanced brucite step edges dissolution (**Fig. 3c, d**). Struvite precipitation however, was not confirmed from Raman spectra. Brucite dissolution releases Mg ions to the solution. The slow diffusion of Mg ions from the reaction interface towards bulk solution results in a thin fluid boundary layer becoming supersaturated with respect to struvite, precipitating subsequently^[15].

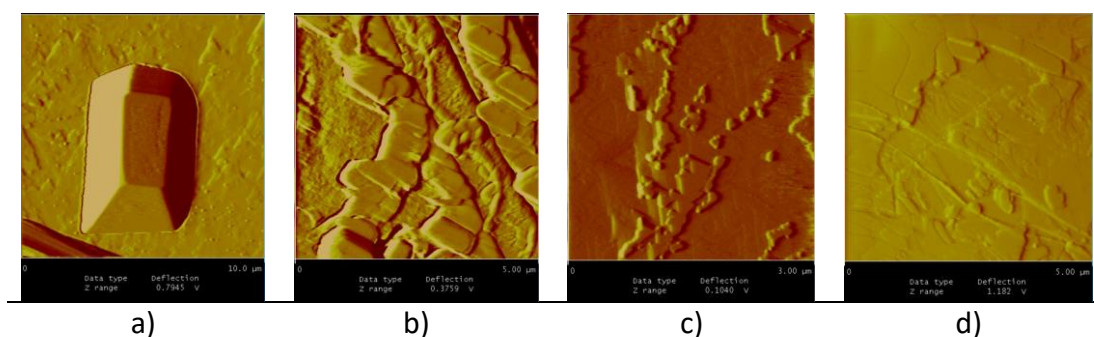


Fig. 3. AFM deflection images showing struvite crystals shaped nanoparticles nucleated on a brucite surface during reaction with solutions of a) b) $(\text{NH}_4)_2\text{HPO}_4$ 500 mM pH 8.5. The differences in brucite morphology in contact with solutions of $\text{NH}_4\text{H}_2\text{PO}_4$ c) 100 mM and d) 500 mM did not reveal struvite precipitation that was confirmed by Raman analysis.

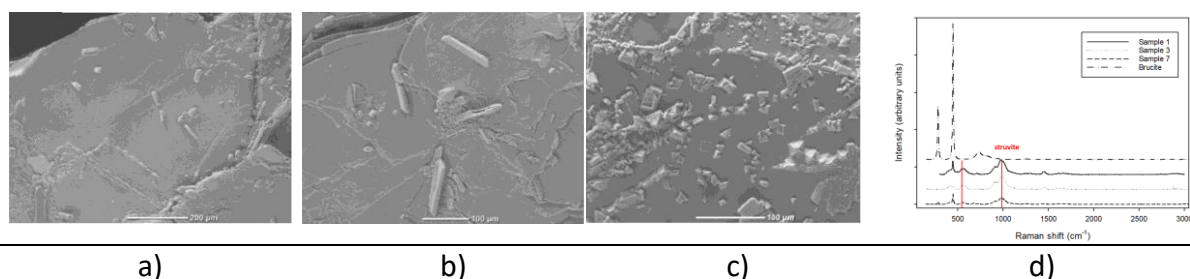


Fig. 4. Scanning electron micrographs of struvite crystals precipitated on brucite surface using solutions of $(\text{NH}_4)_2\text{HPO}_4$ a) 100 mM; b) 15 mM; c) 500 mM and d) Representative Raman spectrums of the new phases showing struvite peaks; (Sample 1, 3, 7 stand for $(\text{NH}_4)_2\text{HPO}_4$ 100 mM, 15 mM and 500 mM, respectively).

CONCLUSIONS. Batch experiments showed that 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. Additionally it is possible to use magnesite as magnesium source to prepare supersaturated solutions from which to recover 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. The presence of suspended magnesite in solutions supersaturated with respect to struvite, at low supersaturations did not induce the precipitation of struvite at the test conditions of the present work. MgO particles quickly convert to Mg(OH)₂ when suspended in water. AFM observations showed that struvite nucleation and crystal growth occurred at step edges of brucite implying dissolution of brucite and release of magnesium ions into the bulk solution. Magnesium-ions accumulation in contact with ammonium and phosphate bearing solutions during flow through experiments evolve enough supersaturation in order for struvite to precipitate. Macro- to nanoscale observations may have implications for the efficiency of using seawater, low grade magnesite and/ or natural or synthetic brucite in struvite recovery processes.

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