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# Struvite precipitation with MgO as a precursor: Application to wastewater treatment

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## HIGHLIGHTS

- A dense MgO suspension is suitable as a precursor.
- The preparation of the suspension hydrates more than 99% of the initial MgO.
- The use of MgO is beneficial to the phosphorous recovery rate.
- Precipitation is highly influenced by the chemistry around the suspended particles.

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## ABSTRACT

Phosphorous (P) is an essential element and plays a key role for life on Earth. It stiffens the bone structure, is a major component of DNA and is involved in the metabolism of living cells. One of the most widely known metabolic processes is photosynthesis, which, amongst many other things, fuels the growth of plants. Modern agriculture uses fertilizers to supply plants with additional phosphorous in order to support photosynthesis and maximize yields. Still today, the primary source for fertilizers is phosphate rock, the supply of which is finite and estimated to be depleted within in the next century. In recent years, several techniques were developed to recycle phosphorous and prevent future scarcity of this vital element. This study examines a method to recover P from nutrient-rich wastewater streams by crystallizing struvite ($MgNH_4PO_4 \cdot 6H_2O$). A low-grade magnesium oxide, a by-product of the magnesite industry, is added to the effluent to precipitate struvite. Precipitation was investigated in terms of the amount of magnesia added, and its influence on crystallization kinetics and the resulting particle morphologies and sizes. The amount of magnesia determines the supersaturation of the solution by fixing the pH and the chemical potential of magnesium ions in solution, thereby inducing crystallization. Here, the use of an MgO suspension couples the struvite precipitation to a prior MgO dissolution step. This step is controlled by surface reaction and it is assumed that the suspended particles facilitate heterogeneous nucleation. Apparently, the amount of magnesia solids has a strong influence and precipitation mainly occurs around the MgO particles.

## 1. Introduction

Today's agriculture is highly dependent on phosphate fertilizers to feed a growing world population with dwindling cultivation areas. Most fertilizers are produced from phosphate ores, and since phosphorous (P) is a limited resource, current reserves are estimated to run out within the next 50 to 100 years (Cordell et al., 2009). To avoid future scarcity, sustainable recovery and recycling techniques are needed to preserve this vital element. One possible approach is the precipitation of struvite, also known as magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4 \cdot 6H_2O$). It can be crystallized from nutrient-rich wastewater that contains high concentrations of ammoniacal nitrogen and phosphate ions, by adding a low-grade magnesium oxide (MgO) as a precursor. This MgO source derives from the magnesite industry, both via recycling and as a by-product (Quintana et al., 2003), is safe and suits agricultural restrictions. Struvite can be used as a slow-release fertilizer and is a potential substitute for conventional fertilizers.

Previous studies (Capdevielle et al., 2013) have investigated the influence of process parameters, and have shown that using highly concentrated MgO suspension is far more useful than using directly the raw and untreated MgO powder bulk material. Consequently, this

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work aims to elucidate the factors that influence this struvite precipitation process. To simplify the conditions, a highly concentrated MgO suspension was introduced in an ammonium dihydrogen phosphate ($H_2NH_4PO_4$-$H_2O$) solution to precipitate struvite. The experiments were performed in an agitated batch reactor as described in Section 2.

The first part of this study focuses on the possibility of using magnesia oxide as a precursor reagent. An investigation was conducted to determine whether the preparation of MgO suspension is reproducible and therefore eligible for further experiments. Full characterization of the suspension includes information about the stability and concentration, which can be gained by investigating sedimentation behavior and determining the weight proportions of the suspension phases. In this study, suspension characterization was followed by monitoring pH and the magnesia ion concentration profile for five identical MgO suspension preparations. All of these repeated suspension preparations showed very similar concentrations and pH profiles, such that it can be assumed that the suspension is at an equal state before every struvite precipitation run. However, it was found that preliminary preparation of the magnesia suspension involves a rather complex hydration mechanism; therefore, further analysis was required to fully understand this mechanism and to examine its final composition.

The second part of this article focuses on the struvite precipitation step. Experiments were conducted to determine how the amount of added magnesia influenced the system. The use of a dense MgO suspension incorporates simultaneous magnesia dissolution and struvite precipitation steps. In order to decouple the two processes and to solely observe the precipitation step, experiments with magnesium chloride solution were conducted under the same conditions as those with magnesia. To ensure the same conditions, the pH was controlled and the amount of dissolved $MgCl_2$ corresponded to the precursor amount of magnesia used in the MgO suspension experiments. Finally, the findings of the $MgCl_2$ solution and the MgO particle experiments were combined to understand the process of struvite precipitation using MgO as a precursor.

## 2. Materials and methods

### 2.1. Magnesia suspension

A concentrated MgO suspension ($80\,gL^{-1}$) was prepared by suspending raw magnesium oxide (light periclase 98%, Panreac) in deionized water. The suspension was stirred (840 rpm) in a double-walled glass reactor (capacity 1 L) with a marine propeller-baffle system at constant 25 °C. The MgO suspension experiments were conducted over a period of 24 h to determine the time at which the pH and the magnesium ion concentration stabilized. Temperature and pH were measured in situ throughout the entire experiment. Samples (6 mL) were taken through the bottom outlet of the reactor, and were immediately filtered with a vacuum flask and membrane filters (pore size 0.2 μm, Whatman Schleicher & Schuell) to obtain the liquid phase. Finally, the remaining suspension was filtered and the solid phase was washed with ethanol. The concentration of magnesium ions ($Mg^{2+}$) was determined over time by analyzing the liquid phase of the samples via ion chromatography (IC-3000, Dionex), using an IonPac™ AS19 column and an IonPac™ CS12 column. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were performed, using a TM 3000 accompanied by a SwiftED3000 X-Stream module (Hitachi), to indicate the composition and surface structure of the MgO suspension product. The results were compared with commercial reference products $Mg(OH)_2$ (95–100.5%, Alfa Aesar), calcined (700 °C), and raw MgO. Thermogravimetric analyses were performed to determine the final conversion of MgO into $Mg(OH)_2$ by means of a SDT Q600 (TA Instrument) with a constant heating rate of $10\,°C\,min^{-1}$ up to 700 °C (Aphane, 2007). Reference mixtures of MgO and $Mg(OH)_2$ with known composition were analyzed, giving a calibration curve that related the determined weight loss to the actual magnesium hydroxide content.

### 2.2. Struvite precipitation

Struvite precipitation runs were carried out in an 8 L batch reactor with a similar setup to the system used for the MgO suspension experiments. The system was agitated (200 rpm) at a constant temperature of 25 °C. The precursors were added to $H_2NH_4PO_4$–$H_2O$ solution maintained at constant initial concentration of $32\,mmol\,L^{-1}$. To investigate the impact of magnesia, the amount of MgO or $MgCl_2$ added to the system was varied to determine its influence on struvite crystallization. Therefore, different volumes of the MgO suspension or 200 mL solutions with an adjusted $MgCl_2$ concentration were added. In this study, the amount of added magnesium is referred to as the molar ratio Mg:P, where Mg is the magnesium amount in all suspended MgO or dissolved $MgCl_2$, and P is the amount of phosphorous in $H_2NH_4PO_4$. The molar ratio also represents the degree of initial supersaturation, meaning that experiments carried out at the same molar ratio are also carried out at the same initial supersaturation. Experiments were conducted out at molar ratios Mg:P of 0.5, 0.75 and 1. All $MgCl_2$ runs were controlled at a constant pH during the entire process by monitoring the pH and titrating a $2.0\,mol\,L^{-1}$ sodium hydroxide solution into the system to compensate for fluctuations in pH. The pH values (range 6.6–8.2, also shown in Fig. 9) were set to the equilibrium pH values of the corresponding precipitation runs with MgO carried out at the same Mg:P ratios.

The experiments lasted up to three hours, and sampling was performed continuously according to the method described previously. Solids, which precipitated after sampling within the liquid phase, were dissolved by adding small amounts of hydrochloric acid. The sample's solid phase was washed with ethanol and dried at ambient temperature. The evolution of $Mg^{2+}$, $NH_4^+$ and $PO_4^{3-}$ concentrations were followed by analyzing the liquid phase via ion chromatography. Crystal size distributions over time were determined via morphogranulometric analysis (Morphologi G3S, Malvern) for every sample. Fourier infrared spectroscopy (Vertex, Bruker) and ion chromatography analysis of previous dissolved solid fractions examined the final composition of the products. EDX and SEM were used to observe the surface properties of the precipitate.

The supersaturation of struvite can be described by the saturation index (SI) shown in the following equation.

$$SI = \log\left(\frac{a_{Mg^{2+}} \cdot a_{NH_4^+} \cdot a_{PO_4^{3-}}}{K_{struvite}}\right) \tag{1}$$

$K_{struvite}$ is the solubility product of struvite and $a_i$ is the species' ion activity. SI was calculated using PHREEQC geochemical software in combination with the Minteq.V4 database (Capdevielle et al., 2013). The program used reaction, mass balances and thermodynamic correlations to model the thermodynamic state of the solutions. As the ion concentrations were relatively low, the Debye–Hückel expression was appropriate to calculate the activity coefficients. The database was updated with the thermodynamic data for struvite, brucite, MgO and $MgOH^+$, which were adopted from the work of Hanhoun et al. (2011). Hence, supersaturations were calculated with PHREEQC from the ion concentration values obtained by ion chromatography (IC).