



## Phosphate recovery through struvite precipitation by CO<sub>2</sub> removal: Effect of magnesium, phosphate and ammonium concentrations

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### ARTICLE INFO

#### Article history:

Received 17 March 2010

Received in revised form

10 November 2010

Accepted 10 November 2010

Available online 18 November 2010

#### Keywords:

Magnesium ammonium phosphate

Precipitation

Scale

Morphology

Crystal growth

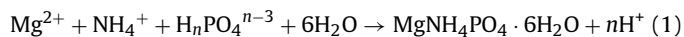
### ABSTRACT

In the present study, the precipitation of struvite (MgNH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O) using the CO<sub>2</sub> degasification technique is investigated. The precipitation of struvite was done from supersaturated solutions in which precipitation was induced by the increase of the solution supersaturation concomitant with the removal of dissolved carbon dioxide. The effect of magnesium, phosphate and ammonium concentrations on the kinetics and the efficiency of struvite precipitation was measured monitoring the respective concentrations in solution. In all cases struvite precipitated exclusively and the solid was characterized by powder XRD and FTIR. The morphology of the precipitated crystals was examined by scanning electronic microscopy and it was found that it exhibited the typical prismatic pattern of the struvite crystals with sizes in the range between 100 and 300 μm. The increase of magnesium concentration in the supersaturated solutions, resulted for all phosphate concentration tested, in significantly higher phosphate removal efficiency. Moreover, it is interesting to note that in this case the adhesion of the suspended struvite crystals to the reactor walls was reduced suggesting changes in the particle characteristics. The increase of phosphate concentration in the supersaturated solutions, for the magnesium concentrations tested resulted to the reduction of struvite suppression which reached complete suppression of the precipitate formation. Excess of ammonium in solution was found favour struvite precipitation. Contrary to the results found with increasing the magnesium concentration in solution, higher ammonium concentrations resulted to higher adhesion of the precipitated crystallites to the reactor walls. The results of the present work showed that it is possible to recover phosphorus in the form of struvite from wastewater reducing water pollution and at the same time saving valuable resources.

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### 1. Introduction

The content of wastewater in pollutants responsible for eutrophication [1] like phosphate and ammonia is in general high and there is urgent need to regulate their concentration levels prior to disposal to aquatic reservoirs. Eutrophication may also occur in nature provided that there is abundance of nutrients stimulating plant growth in lakes, estuaries, or slow-moving streams. Phosphate and ammonia can be removed simultaneously in the presence of magnesium through by precipitation as the sparingly soluble magnesium ammonium phosphate salt, known as struvite (MgNH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O) [2,3]. Struvite crystals are white in color with orthorhombic habit and precipitate according to reaction (1) [4]:



with  $n = 0, 1$  and  $2$ , depending on the solution pH, which regulates the distribution of the various phosphate species.

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Key parameters controlling the precipitation process of struvite from the respective supersaturated solutions, include solution pH [5,6], temperature [6], rate of stirring [7,8], supersaturation [9,10], nature of materials [11,12] and the presence of foreign ions including calcium [8,13] and sulphate [14]. Ali [15] investigated struvite precipitation using thermodynamic models and simulation processes in which all equilibria were taken into consideration. In aqueous solutions containing dissolved magnesium, ammonium and phosphate ions a number of complexes are formed which result in the reduction of the concentrations of the free ions (Mg<sup>2+</sup>, NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup>) which are the constituents of the crystalline precipitate. Abbona et al. [6] studied the effect of pH and concentration and of the corresponding supersaturation ratios,  $\beta_S$  and  $\beta_N$ , of struvite and newberyite (MgHPO<sub>4</sub>), respectively, on the crystallization of these two magnesium phosphate compounds. They showed that when  $\beta_N/\beta_S < 2$ , struvite always crystallizes first, whereas for  $\beta_N/\beta_S > 4$  the precipitation of newberyite precedes.

The effect of magnesium concentration in the supersaturated solutions on the precipitation of struvite has been widely investigated [16,17]. However, the effect of phosphate concentration on struvite precipitation has not been adequately investigated so far,

especially in cases where magnesium concentration was kept constant in a series of experiments. Quintana et al. [17] showed that the yield of struvite, precipitated by magnetic stirring and aeration, increased upon increasing magnesium concentration in solution. Pastor et al. [18] showed that higher than 80% of phosphorus was removed through struvite precipitation in a stirred reactor. This efficiency could be improved by increasing the  $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$  molar ratio. Lee et al. [19] showed that adding less than 0.05 M of both magnesium and phosphate salt or more than  $\sim 0.07$  molar ratio of magnesium with respect to total nitrogen resulted in the continuous formation of struvite during the composting process of swine manure.

The recovered ammonium and phosphate through struvite crystallization can be used efficiently as a valuable mineral fertilizer for plants. On the other hand however severe scaling problems because of the formation of struvite deposits in pipes, pumps and screens in wastewater treatment plants (WWTP) have been reported [11,12]. The determination of the experimental conditions for maximum phosphate removal efficiency from wastewater effluents without at the same time forming undesirable scale on WWTP equipment, is of paramount importance.

Carbon dioxide stripping could be applied to struvite crystallization [20,21].  $\text{CO}_2$  removal from the aqueous solutions results to the increase of pH. Since the solution supersaturation with respect to struvite increases drastically upon increasing the solution pH, struvite precipitation is favoured, thus reducing the need to increase solution pH by the addition of alkali [22]. The removal efficiency of the  $\text{CO}_2$  stripper depends on several parameters, i.e., the characteristics of the influent, including total alkalinity, temperature, initial concentration of dissolved  $\text{CO}_2$  gas and influent flow rate, effluent recycle rate and aeration rate [23]. In an earlier report by our research group [24] the effects of the airflow rate and solution pH on struvite precipitation by the dissolved  $\text{CO}_2$  degasification technique were presented. It was shown that the phosphate removal efficiency could be improved by increasing the airflow rate to  $25 \text{ L min}^{-1}$ , or by increasing the initial solution pH for higher air flow rates [24]. In the present work, in an attempt to ameliorate phosphorus removal through struvite precipitation avoiding scale formation, the effect of magnesium, phosphate and ammonium concentrations in the supersaturated solutions on struvite precipitation were investigated. Experiments were done in which magnesium concentrations were increased while phosphate concentration was kept constant. In a second series of experiments phosphate and ammonium concentrations in solutions were varied for given, constant magnesium concentration in the supersaturated solutions.

## 2. Materials and experimental methods

The experimental solutions were prepared by mixing accurately measured volumes of magnesium chloride, ammonium dihydrogen phosphate (or alternatively potassium dihydrogen phosphate and ammonium chloride) stock solutions in a  $50 \text{ mg L}^{-1}$   $\text{CaCO}_3$  solution. The solutions were prepared from the crystalline solids:  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (Fluka, >99%),  $\text{NH}_4\text{H}_2\text{PO}_4$  (Fluka, >99%)  $\text{KH}_2\text{PO}_4$  (Sigma–Aldrich, >99%) and  $\text{NH}_4\text{Cl}$  (Sigma–Aldrich, >99%) dissolved in distilled water. The  $50 \text{ mg L}^{-1}$   $\text{CaCO}_3$  solution was prepared by dissolving the appropriate amount of solid calcium carbonate (Merck, >99%) in distilled water by  $\text{CO}_2$  bubbling at atmospheric pressure till saturation of the solution with  $\text{CO}_2$ . Next, the dissolved carbonate was removed bubbling atmospheric air through the solution using a sparger for better dispersion of the gas into the aqueous phase.

Past pH adjustment to an initial value of 6.5 with 1 M NaOH solution, 600 mL of the experimental solution were introduced in a 1 L

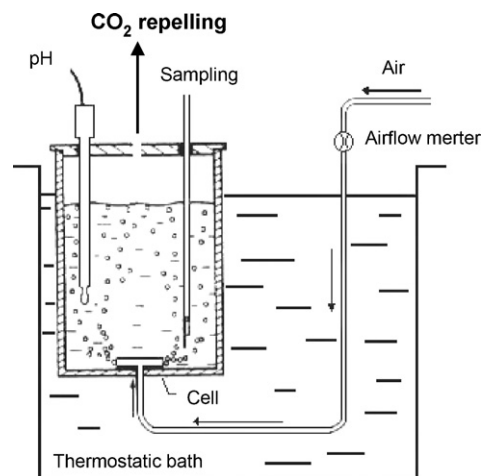


Fig. 1. Schematic experimental setup of the dissolved carbonate removal technique.

cylindrical polyvinyl chloride (PVC) reactor covered with a lid from the same material, bearing ports for sampling, air sparger, sensors, etc. The struvite precipitation was induced by the dissolved  $\text{CO}_2$  degasification technique. Bubbling the air supply through the solution resulted in the increase of the solution pH to higher values. Depending on the concentration of the magnesium, phosphate and ammonium in solution, struvite precipitation was initiated spontaneously at the appropriate pH value corresponding to a critical value of supersaturation with respect to struvite. Airflow through the reactor was controlled and monitored by a precalibrated airflow meter. The solution temperature was controlled by a thermostat with circulating water. The solution pH in the reactor was monitored with a combination glass/Ag/AgCl electrode, calibrated with the appropriate standard buffer solutions. A schematic illustration of the experimental setup is given in Fig. 1.

All experiments were carried out at a fixed airflow rate of  $40 \text{ L min}^{-1}$ . It was shown that the yield of struvite decreased upon increasing solution temperature from 25 to  $60^\circ\text{C}$  [25]. All experiments were done at  $25^\circ\text{C}$ . A series of experiments was done for the investigation of the effect of magnesium concentration in the supersaturated solutions on the precipitation of struvite. In this series of experiments various increasing magnesium concentrations were used for the initial phosphorus concentration was  $130.2 \text{ mg L}^{-1}$ . The  $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$  molar ratio varied from 1 to 5. In a second series of experiments, phosphate concentration in the solutions varied while the magnesium concentration was kept constant and equal to  $92.3 \text{ mg L}^{-1}$ . In this series of experiments, ammonium and phosphate ions were added as  $\text{NH}_4\text{H}_2\text{PO}_4$  so that the molar ratio  $\text{N}:\text{H}_n\text{PO}_4^{n-3}$  was equal to 1:1. The  $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$  molar ratio varied from 1/5 to 5. Finally, a third series of experiments were carried out in which initial magnesium concentration was  $130.2 \text{ mg L}^{-1}$  while ammonium concentration in solution varied, in order to investigate the effect of this parameter as well. For these experiments, magnesium, ammonium and phosphate ions were added as  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NH}_4\text{Cl}$  and  $\text{KH}_2\text{PO}_4$ , respectively. The molar ratio  $\text{Mg}:\text{H}_n\text{PO}_4^{n-3}$  was kept equal to 1:1 and the  $\text{NH}_4^+/\text{H}_n\text{PO}_4^{n-3}$  molar ratio varied from 1/4 to 3 (corresponding to ammonium concentration in the range  $18.93\text{--}227.27 \text{ mg L}^{-1}$ ). In all experiments, samples were withdrawn periodically, filtered through  $0.45 \mu\text{m}$  membrane filters and the filtrates were analyzed for phosphate spectrophotometrically [26]. At the end of each experiment, the solution was filtered through  $0.45 \mu\text{m}$  membrane filters and the solid precipitates were characterized by powder X-ray diffraction (XRD), Fourier transform infra-red (FTIR) and scanning electron microscopy (SEM). XRD was carried out at room temperature with a Philips X'PERT PRO diffractometer in step scanning mode using

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