Temperature impact assessment on struvite solubility product: A thermodynamic modeling approach

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ABSTRACT

This work addresses the problem of phosphorus recovery from wastewater by struvite precipitation, which is chemically known as magnesium ammonium phosphate hexahydrate $MgNH_4PO_4 \cdot 6H_2O$. The struvite solubility product values that are reported in the literature were found to vary significantly, from one solution to another and over the range of the experimental conditions as well. The various factors affecting the struvite solubility include pH, ionic strength and temperature. The struvite solubility product is yet a very important parameter to determine the supersaturation ratio.

A thermodynamic model for phosphate precipitation is proposed to determine the phosphate conversion rate and the value of struvite solubility product for a temperature range between 15 and 35 °C. This model is based on numerical equilibrium prediction of the study system $Mg–NH_4–PO_4–6H_2O$. The mathematical problem is represented by a set of nonlinear equations that turns, to an ill-conditioned system mainly due to the various orders of magnitude of the involved variables. These equations have first been solved by an optimization strategy with a genetic algorithm to perform a preliminary search in the solution space. The procedure helps to identify a good initialization point for the subsequent Newton–Raphson method. A series of experiments were conducted to study the influence of pH and temperature on struvite precipitation and to validate the proposed model.

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1. Introduction

Wastewater discharges of nitrogen and phosphorus to the environment have produced an increase in water pollution because these nutrients accelerate eutrophication, producing detrimental consequences for aquatic life as well as for water supply for industrial and domestic uses.

One proposed solution to this problem is the recovery of nutrients using precipitation. Two major precipitation schemes have been developed for phosphorus recovery from wastewater, involving either the so-called calcium phosphate (CP) or magnesium ammonium phosphate (MAP), i.e., struvite.

The struvite forms according to the following reaction [1]:
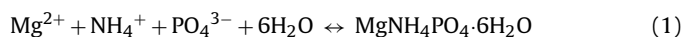
$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \leftrightarrow MgNH_4PO_4 \cdot 6H_2O \tag{1}$$

Struvite precipitation from wastewater effluents is seen as an alternative to traditional biological and chemical phosphorus removal processes that have been widely used in the wastewater treatment industry and has gained increasing interest.

Struvite is known to cause some problems on equipment surfaces of anaerobic digestion and post-digestion processes in the wastewater treatment industry (especially biological nutrient removal processes) through major downtime, loss of hydraulic capacity, and increased pumping and maintenance costs [2]. Although struvite can be viewed as a problem in wastewater treatment plants, the conditions for its formation found within the environment of wastewater treatment works can be exploited for extraction of struvite, as a commercial product. Struvite can be used as a slow release fertilizer at high application rates, without the danger of damaging plants [3–6].

Struvite formation occurs relatively quickly because of the presence of excess supersaturation in the liquid, as a result of the chemical reaction of magnesium with phosphate in the presence of ammonium.

Predicting struvite precipitation potential, yield and purity is thus of major importance for reactor design and operation for struvite precipitation.

Table 1
Reported experimental values of the K_{sp} for struvite (25 °C).

pK_{sp}	K_{sp}	Reference
13.15	7.08×10^{-14}	Taylor et al. [14]
9.41	3.89×10^{-10}	Borgerding [15]
12.60	2.51×10^{-13}	Snoeyink and Jenkins [16]
13.12	7.59×10^{-14}	Burns and Finlayson [17]
9.94	1.15×10^{-10}	Abbona et al. [18]
13.27	5.37×10^{-14}	Ohlinger et al. [11]

Supersaturation may be developed by increasing the aqueous medium content in ammonium, magnesium or orthophosphate and/or pH. Although H^+ concentration does not directly enter the solubility product equation for struvite, struvite precipitation is highly pH dependent.

Several chemical equilibrium-based models have been developed and allow reasonable prediction of struvite precipitation [7–12]. These models are based on physicochemical equilibrium of the various ionic, dissolved, and solid species. A struvite precipitation model at least requires the incorporation of concentrations of ionic species NH_4^+, PO_4^{3-}, and Mg^{2+}, dissolved species NH_3 and H_3PO_4, and solid species $MgNH_4PO_4$. However, a number of other ionic species (e.g., HPO_4^{2-}, $H_2PO_4^{2-}$, $MgOH^+$, $MgPO_4^-$, $MgH_2PO_4^+$), dissolved species (e.g., H_3PO_4, $MgHPO_4$), and solid species (e.g., $Mg_3(PO_4)_2 \cdot 8H_2O$, $Mg_3(PO_4)_2 \cdot 22H_2O$, $Mg(OH)_2$, $MgHPO_4$) exist in equilibrium. Finally, it must be highlighted that the complexity of models depends on the number of soluble and solid species considered.

Loewenthal et al. [7] considered struvite as the only solid phase to precipitate from synthetically prepared solutions: ionic species considered were Mg^{2+}, NH_4^+, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^{2-}$, and dissolved species were NH_3 and H_3PO_4. In addition to the above H_2CO_3, CH_3COO^-, CH_3COOH, carbonate, and bicarbonate were also considered. Harada et al. [8] developed a model to predict struvite formation in urine. The solid species involve calcium precipitates $Ca_3(PO_4)_2$, $CaHPO_4$, $Ca(OH)_2$, $CaCO_3$ and $CaMg(CO_3)_2$ as well as those containing Mg, namely, struvite, $Mg(OH)_2$, and $MgCO_3$. As the number of solid and soluble species considered increases, the complexity of the induced model also increases. This explains why analytical solutions are no longer viable and hence numerical solution is needed. Ohlinger et al. [11] included ionic strength effects and considered only struvite as the solid species in their model (MINTEQA2). They also took into account $MgH_2PO_4^+$ and $MgPO_4^-$ and used an iterative technique to converge one concentration value to an experimentally measured value, while the other concentrations were computed from equilibrium expressions. Wang et al. [12] included formation of $Mg(OH)_2$ solid in addition to struvite and also considered $MgHPO_4$ as a dissolved species. Buchanan et al. [13] used an aquatic chemistry equilibrium model (MINTEQA2; EPA, 1991) to model struvite formation.

It must be yet emphasized that discrepancies still exist between the reported values (Table 1) of the solubility product (K_{sp}) for struvite.

From the analysis of the literature, it can be said that possible reasons for dispersed K_{sp} or pK_{sp} values can be attributed to different factors: values may be derived from approximate solution equilibria; the effect of ionic strength is often neglected; mass balance and electroneutrality equations are not always used; different chemical species are selected for the calculations.

It must be also said that pK_{sp} uncertainty influences the conversion rate of struvite, as demonstrated by Montastruc et al. [19]. This is an important point for process design and was calculated in this study.

The standard methods for the experimental determination of a K_{sp} value of a particular reaction involve either the formation of a precipitate or the dissolution of a previously formed salt in distilled water. Although temperature has a lower impact on struvite precipitation than other parameters such as pH and supersaturation [4], it can yet influence struvite solubility.

Only a few works were devoted to temperature influence on struvite precipitation. Aage et al. [20] determined the struvite solubility product with a radiochemical method at various temperatures. Burns and Finlayson [17] used pH and concentration measurements to investigate the influence of temperature on the solubility product of struvite. The activity coefficients and ionic concentrations of species were calculated by EQUIL, a Fortran computer program used for chemical equilibrium computation. According to these results, a steady increase in solubility is observed with an increase in temperature.

From a practical point of view, the K_{sp} value depends, on the one hand, on the experimental precision, and on the other hand on the thermodynamic method used to calculate the equilibrium constant values, at different temperatures, for all the equilibrium relations involved during the precipitation of struvite.

It is important to highlight that the final values of K_{sp} presented in the dedicated literature are dramatically impacted by the conditions and assumptions associated with the thermodynamic data. Table 1 illustrates the variation range of K_{sp} values proposed by several authors. The published pK_{sp} values at 25 °C range from 9.41 to 13.27.

In that context, the objective of this paper is to propose the development of a rigorous thermodynamic model based on a known and reliable database with a unified framework for struvite K_{sp} determination that will be consistent at different temperatures from experimental values, using a robust numerical method. This approach will serve to identify the species that will precipitate and the associated thermodynamical constants in a typical process scale.

The paper is organized as follows:

First, the experiments to determine the solubility product of struvite from a synthetic solution at various temperatures are presented. They were conducted in a stirred reactor at 15, 20, 25, 30 and 35 °C to determine the efficiency of struvite precipitation from a synthetic wastewater solution. XRD analysis of the formed precipitates demonstrated the high purity of the struvite crystals for pH values lower than 10. The next step consists in the computation of the thermodynamic solubility product K_{sp} and of the conversion rate of phosphate.

The second part of this paper then presents the development of a thermochemical model, suited to struvite precipitation at various temperatures using a Davies activity coefficient modeling approach [21]. The mathematical problem is represented by a set of nonlinear equations. A two-step solution strategy is proposed, combining a genetic algorithm for initialization purpose followed by a standard Newton–Raphson method implemented within MATLAB environment. This method gives a robust initialization to treat this kind of problem for any initial conditions. Let us recall that genetic algorithms were previously successfully used in a related problem for the resolution of a thermochemical equilibrium model involved in calcium phosphate precipitation for initialization purpose of a Gibbs energy minimization problem [19].

2. Materials and methods

Experiments were carried out at different temperatures 15, 20, 25, 30, 35 °C in a stirred reactor (1 l) at a rotational speed around 500 rpm. Stock solutions of magnesium and ammonium phosphate were prepared from corresponding crystalline solids, i.e., $MgCl_2 \cdot 6H_2O$ and $NH_4H_2PO_4$. Deionised water was used to prepare