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REMOVAL OF PHOSPHATE FROM SYNTHETIC WASTEWATER BY STRUVITE PRECIPITATION IN A STIRRED REACTOR

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ABSTRACT

The cost of environmental protection and pollution prevention is increasing, above all because of stringent effluent quality standard. In that context, phosphorus impact on water pollution plays a major role because it accelerates eutrophication. This work addresses the problem of phosphorus recovery from synthetic wastewater by struvite precipitation. The general objective is to develop a methodology for an optimal design of an automated pilot reactor for the treatment of wastewater. In this perspective, preliminary precipitation experiments were carried out at laboratory scale to examine the effects of final pH, magnesium and phosphate concentrations in the influent. A thermodynamic model for struvite precipitation is proposed involving Davies activity coefficients.

Keywords: Struvite, Precipitation, P-recovery, Stirred reactor, Modelling**.**

INTRODUCTION

Wastewater discharges of nitrogen and phosphorus to the environment have produced an increase in water pollution because these nutrients accelerate eutrophication, producing grave 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 precipitations have been developed for phosphorus recovery from wastewater, involving either the so-called calcium phosphate (CP) or magnesium ammonium phosphate (MAP), i.e., struvite.
Struvite is a white crystalline substance consisting of magnesium, ammonium and phosphorus in equal molar concentrations ($MgNH_4PO_4$-$6H_2O$). Struvite forms according to the general reaction shown below (Bouropoulos and Koutsoukos, 2000):

$$Mg^{2+}+NH_4^{+}+PO_4^{3-}+6H_2O \rightarrow MgNH_4PO_4, 6H2O$$

Struvite crystallisation from wastewater effluents is seen as an alternative to traditional biological and chemical phosphorus removal processes widely used in the wastewater treatment industry. It presents the advantage of not only

removing phosphorus but also generating a compound that could be reused as a commercial fertilizer (Durrant et al., 1999; Nelson et al., 2003). 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. Supersaturation may be developed by increasing the aqueous medium content in ammonium, magnesium or orthophosphate and/or pH.
For this study, batch experiments were conducted to determine the efficiency of struvite precipitation in synthetic wastewater. More particularly, the influence of the following parameters was investigated: pH, magnesium and phosphate concentration. The experimental results are compared with those obtained by a thermochemical model, enough representative of struvite precipitation using a Davies activity coefficient modeling (Hanhoun et al., 2009). This is a first step towards the development of a model taking into account kinetics of struvite precipitation.

MATERIALS AND METHODS

A series of batch investigations was conducted to study the influence of species concentration and pH on struvite precipitation. Experiments were carried out at 25°C in a 500 ml stirred vessel. Stock solutions of magnesium and ammonium phosphate were prepared from corresponding crystalline solids $MgCl_2.6H_2O$ and $NH_4H_2PO_4$. Deionised water was used to prepare the synthetic wastewater solution. The supersaturated solutions (corresponding to a final phosphorus concentration of 4 mM with an $Mg/NH_4/PO_4$ molar ratio equal to 1) were prepared by a rapid agitation of $NH_4H_2PO_4$ and pH was then adjusted (by the addition of the appropriate amount of a standard solution of sodium hydroxide), followed by the addition of the appropriate volume of stock magnesium chloride solution. Finally, pH was adjusted again as needed. Experiments were performed at several pH values [7-11.5] and keep constant all over the period of the reaction (1 hour). The homogeneity of the solution was performed by a magnetic stirrer. Other experimental runs were carried out in the same way with a final phosphorus concentration of 20 mM.
The formed precipitate was collected by filtration through a 0.2 mm membrane filter and dried at ambient temperature. Residual concentrations of Mg^{2+} (respectively PO_4^{3-}) ions in solution after filtration were analysed by atomic absorption (AA) (respectively by spectrophotometry). X-Ray Diffraction (XRD) was used to determine the composition of the precipitate produced. Further samples of precipitate were dissolved in nitric acid: these samples were analysed for magnesium and phosphorus concentrations. The theoretical concentrations were calculated from the dissolved mass assuming that the formed precipitate is pure struvite.

Results

Figure 1 shows the results of an X-Ray Diffraction analysis performed on the formed precipitate. The presence of struvite is indicated by the location of the intensity peaks, corresponding to the standard database lines for struvite.

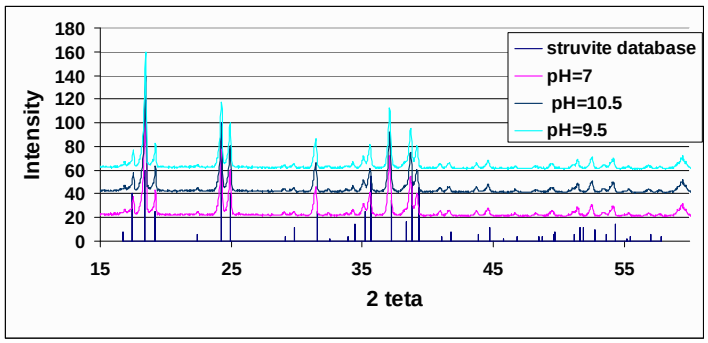

Figure 1. X- ray diffraction analysis results of formed precipitate from the synthetic solutions at different pH values and comparison with values from struvite database.

The results show that only the peaks of struvite were found in the investigated pH range [7-10.5]. They were further confirmed by comparison with solid analysis of phosphate/magnesium. It must be yet pointed out that other precipitates may occur as reported in (Bouropoulos and Koutsoukos, 2000) with pH values above 10.5, where a visible floculation of crystals is observed with the precipitation of $Mg_3(PO_4)2.22H_2O$. Identical phenomena were confirmed within the same pH range in other studies (Lee et al., 2003; Le Corre et al., 2007).

CHEMICAL EQUILIBRIUM MODEL FOR STRUVITE PRECIPITATION

In this work, a thermodynamic model for struvite precipitation is proposed, based on Davies model of activity coefficients taking into account various phases which can precipitate in the range of pH to be considered. The model determines the phosphate conversion rate and is based on numerical equilibrium prediction of the study system Mg-NH_4-PO_4-$6H_2O$. The parameters include the solubility product of struvite. The model involves, on the one hand, the mass balances for magnesium, ammonium and phosphate as a function of conversion rate and the electroneutrality equation, on the other hand (Montastruc et al., 2003). As reported elsewhere, the thermodynamic model (Hanhoun et al., 2009) uses the following equilibrium constants (see Table 1)

Table 1. Equilibrium constants for complexes presented in the equilibrium equations. (Hanhoun et al 2009).

Equilibrium	Value
$H_2PO_4^- + H^+ \leftrightarrow H_3PO_4$	$10^{-2.15}$
$HPO_4^{2-} + H^+ \leftrightarrow H_2PO_4^-$	$10^{-7.20}$
$PO_4^{3-} + H^+ \leftrightarrow HPO_4^{2-}$	$10^{-12.35}$
$H_2PO_4^- + Mg^{2+} \leftrightarrow MgH_2PO_4^+$	$10^{-0.45}$
$HPO_4^{2-} + Mg^{2+} \leftrightarrow MgHPO_4$	$10^{-2.91}$
$PO_4^{3-} + Mg^{2+} \leftrightarrow MgPO_4^-$	$10^{-4.80}$
$OH^- + Mg^{2+} \leftrightarrow MgOH^+$	$10^{-2.56}$
$H^+ + NH_3 \leftrightarrow NH4^+$	$10^{-9.25}$
$H_2O \leftrightarrow H^+ + OH^-$	10^{-14}
$NH4^+ + PO_4^{3-} + Mg^{2+} \leftrightarrow MgNH_4PO_4.6H2O$	$10^{-13.26}$

RESULTS AND DISCUSSION

The experimental results have been compared with the values predicted by the thermodynamical model for pH several values [7-10.5], as displayed in Figures 2 and 3.

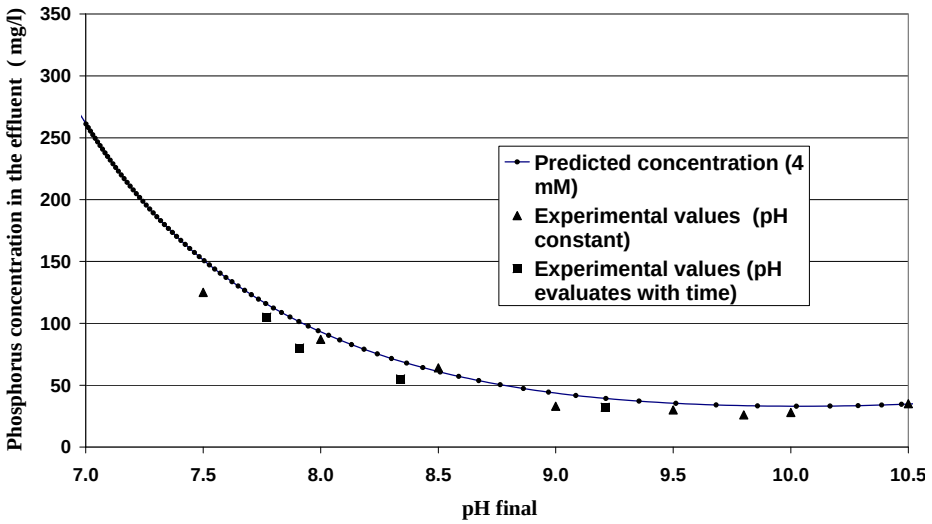

Figure 2. Comparison between the experimental values and the results of the thermochemical model. (Low concentration 4 mM)

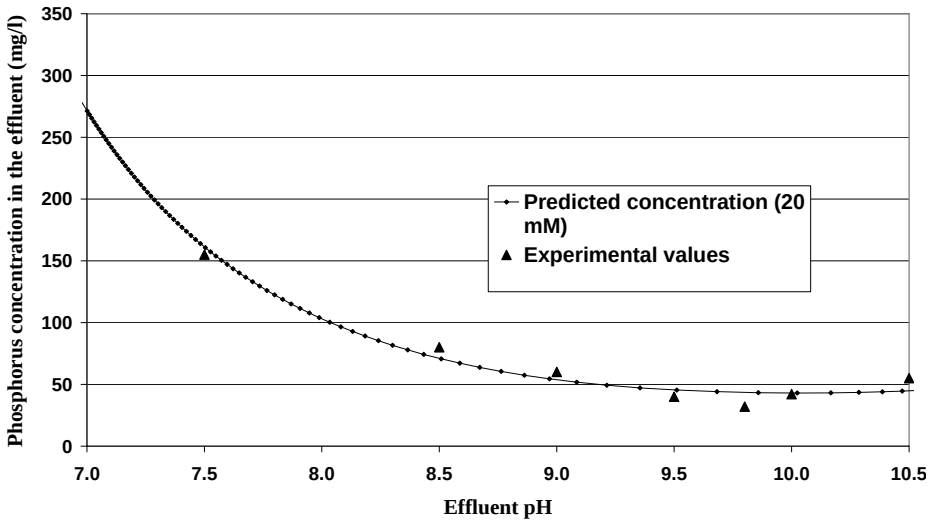

Figure 3. Comparison between the experimental values and the precipitation model.(high concentration 20 mM)

It can be seen that the experimental values are in agreement with the computed results. Optimum experimental pH for struvite precipitation is 9.8, which corresponds to a phosphorus removal of 80% (respectively 94.8%) for an initial concentration of 4 mM (respectively 20mM). This experimental result is identical to the value reported in the literature (Booker et al., 1999).

It can be thus concluded that the developed model allows to predict thermodynamic equilibrium of struvite production for a pH range between 7 and 10.5. It will be used as a part of the thermodynamic core model for the studied precipitation process. The process design yet requires knowledge of struvite crystal growth and an establishment of kinetic models. For this reason, another experiment was carried out in a stirred reactor (1L), with an initial concentration of PO_4, Mg, NH_4 of 4 mM, to study the effect of initial pH on struvite precipitation kinetics. During this experimental run, pH was not set at a fixed value as previously: only initial pH was controlled [8.5-10] and its evolution with time was measured (see figure 4). The measurement of Mg and P final concentrations exhibits a molar ratio approximately equal to unity, thus demonstrating the exclusive formation of struvite for each experiment. The phosphorus residual content was also compared with the value computed by the model as displayed in Figure 4.

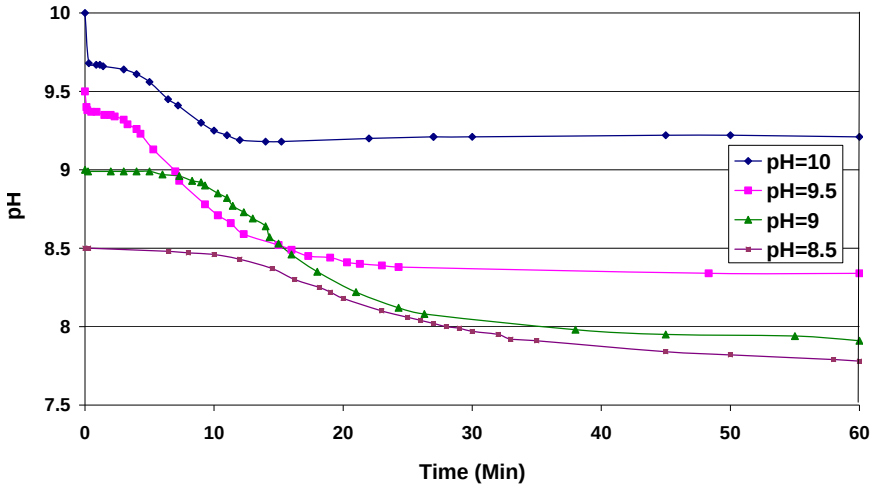

Figure 4. Average pH versus time for initial pH values

It must be highlighted that the observed induction time was affected by variations in initial pH. For example, for an initial pH value equal to 9, the solution became cloudy after 6 minutes, whereas the first particles were visible only after 20 seconds at pH 10.
The result presented here showed that pH is an efficient measurement that can be used for the prediction of the kinetics of struvite precipitation. The pH drop that was typically observed during struvite precipitation reflects the rates at which struvite crystals may nucleate.

CONCLUSIONS AND PERSPECTIVES

This research investigated the potential of struvite precipitation as a method to recover phosphorus from wastewater, while concurrently removing ammonium and magnesium. For high pH values [7-10.5], a domain in which struvite precipitation can occur is observed. For this purpose, this study has presented a

thermodynamic model for struvite precipitation: the obtained results have shown that an increase in pH enhances precipitation efficiency, with a predicted maximum precipitation rate at a pH value equal to 9.8. The model validity was checked for a pH range between 7 and 10.5, with a strong hypothesis based on a struvite exclusive formation. This assumption is validated by XRD analysis for pH-constant experiments, and for free pH experiments by Mg and PO_4 measurements.
The thermodynamic model developed in this study will now be embedded in a modelling framework for determination of process operating conditions for struvite precipitation in a stirred reactor.

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