A comprehensive computational approach to identify the effect of ligands on struvite crystallization

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SUMMARY

This paper primarily focused on the struvite process design based on solution by thermodynamics and kinetics. Struvite is a crystal and its chemical composition is $MgNH_4PO_4 \cdot 6H_2O$. The predominant parameters involved in thermodynamic are thermodynamic equilibria and pH value. The main solution involved in chemistry are the complex formations between Mg, NH_4 and PO_4, which include Mg^{2+}, $MgOH^{[]}$, $MgH_2PO_4^+$, $MgHPO_4$, $MgPO_4$, H_3PO_4, $H_2PO_4^{[]}$, $PO_4^{3[]}$, $MgHPO_4$, $MgPO_4^{[]}$, NH_3. The kinetics parameters involved in this modelling are the mass deposition, size of the growing crystal etc. The modelling approach was conducted in fed-batch condition. This paper then focused on the inclusion of thermodynamic equilibria to identify the effect of ligand on struvite growth kinetics as well as solution chemistry. This modelling approach included citrate as a ligand. The simulation approach was conducted using gPROMS process simulation package.

Key words: *struvite, process, modelling, simulation, fed-batch, ligands.*

1. INTRODUCTION

The use of metal ion buffers in various aspect of environmental and reaction engineering are well known. The use of metal ion buffers provides a controlled source of free metal ions in biological nutrient media at essentially constant levels. The maintenance of constant free level of metal ions is also useful to control the metal ions action in many industrial chemical processes.

The controlled supply of metal ions is due to the complex formation between organic ligands and active metal ions, when ligands exist in sufficient concentrations. The metal complexing capacity of the organic ligand depends on pH and it decreases as the solution is made ore acidic (Perrin and Dempsey 1974). Among the first complexing agents used in this way were citrate and tartrate ions, but more recently EDTA,

DTPA and NTA have become the chelating agent of this choice (Perrin and Dempsey 1974; van der Houwen and Valsami-Jones 2001). It is worthwhile pointing out that the organic ligands sometimes are known as chelating agent in literature.

A novel use of organic ligand is in the crystallization process to maintain constant controlled supply of metal ions, when the source solution is highly concentrated (Perrin and Dempsey 1974; Srinivasan et al. 2002). Van der Houwen and Valsami-Jones (2001) used citrate for controlled HAP crystallization. Srinivasan et al. (1999, 2002) used EDTA for controlled KAP crystallization. The use of chelating agent is to maintain controlled supersaturation by decreasing the level of supersaturation so that crystals grow instead of rapid precipitation. This is done due to the increase of metastable zone width in the presence of organic ligands (Perrin and Dempsey 1974).

2. STRUVITE AND ITS MODELLING APPROACH

Struvite is one type of crystal, which forms in nutrient rich wastewater in supersaturated condition. Struvite consists of magnesium, ammonium and phosphate ions. Solution chemistry plays a predominant role in struvite crystal formations. In supersaturated solution, struvite is formed by chemical reaction of the free Mg^{2+}, NH_4^+ and PO_4^{3-} as demonstrated:

$$Mg^{2+} + NH_4^+ + PO_4^{3-} \Leftrightarrow MgNH_4PO_4 \quad (1)$$
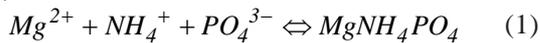
Studies of preferential struvite accumulation were carried out using nutrient rich field effluents (Perrin and Dempsey 1974; van der Houwen and Valsami-Jones 2001). Ohlinger (2000) also describes a steady-state model of struvite deposition, based on the change of struvite's solubility product. A nucleation model and kinetic study were described, to determine the rate constant for struvite precipitation, in anaerobic swine lagoon effluent (Nelson 2000; Nelson et al. 2003) to determine reaction order and rate constant using traditional reaction rate kinetic models. However, the models described by Ohlinger (1999); Ohlinger et al. (2000) and Nelson et al. (2003) offered little understanding of the actual growth rate of struvite. Battistoni et al. (2001) described a nutrient removal system based on hydroxyapatite crystallisation in a fluidized bed reactor. Harrison (1995) described the dependency of struvite growth kinetics on solution pH and supersaturation. In order to rigorously design a struvite removal system, it is necessary to understand crystal growth kinetics relating to all possible influences.

3. MATHEMATICAL MODELLING AND FORMULATION

The key parameters involved in struvite solution chemistry are solution supersaturation, pH, and initial concentration of the reactants. Solution, consisting of *Mg*, *NH₄* and *PO₄*, remains in complex forms of $Mg2^+$, $MgOH^-$, $MgH_2PO_4^+$, $MgHPO_4$, $MgPO_4$, H_3PO_4, $H_2PO_4^-$, PO_4^{3-}, $MgHPO_4$, $MgPO_4^-$, NH_3 (Ohlinger 1999; Bouropoulos and Koutsoukos 2000). The basic thermodynamic relations of chemical complexes are given in Table 1.

Table 1. Thermodynamic equilibria of struvite solution chemistry

Thermodynamic equations	pK value	References
$\{MgOH^+\} \Leftrightarrow \{Mg^{2+}\} + \{OH^-\}$	$10^{-2.56}$	*Childs 1970*
$\{NH_4^+\} \Leftrightarrow \{NH_3(aq)\} + \{H^+\}$	$10^{-0.45}$	*Martell et al. 1993*
$\{HPO_4^{2-}\} \Leftrightarrow \{H^+\} + \{PO_4^{3-}\}$	$10^{-12.35}$	*Morel and Hering 1993*
$\{H_2PO_4^{2-}\} \Leftrightarrow \{H^+\} + \{HPO_4^{2-}\}$	$10^{-7.20}$	*Morel and Hering 1993*
$\{H_3PO_4^{2-}\} \Leftrightarrow \{H^+\} + \{HPO_4^{3-}\}$	$10^{-2.15}$	*Martell et al. 1998*
$\{MgH_2PO_4^+\} \Leftrightarrow \{Mg^{2+}\} + \{H_2PO_4^-\}$	$10^{-0.45}$	*Martell et al. 1993*
$\{MgHPO_4^+\} \Leftrightarrow \{Mg^{2+}\} + \{HPO_4^{2-}\}$	$10^{-2.91}$	*Martell et al. 1993*
$\{MgPO_4^+\} \Leftrightarrow \{Mg^{2+}\} + \{PO_4^{3-}\}$	$10^{-4.80}$	*Martell et al. 1993*

The total constituents concentration for *Mg*, *NH₄* and *PO₄*, denoting $C_{T, Mg}$, C_{T, NH_4}, C_{T, PO_4}, are the total ionic concentration of their complexes and free ions as illustrated:

$$C_{T,PO_4} = [H_3PO_4] + [H_2PO_4^{2-}] + [PO_4^{3-}] + [MgH_2PO_4^+] + [MgHPO_4] + [MgPO_4^-] \quad (2)$$

$$C_{T,Mg} = [Mg^{2+}] + [MgOH^+] + [MgH_2PO_4^+] + [MgHPO_4] + [MgPO_4] \quad (3)$$

$$C_{T,NH_4} = NH_3(aq) + [NH_4^+] \quad (4)$$

The thermodynamic equations, described above, interact the pH value of the solution due to the presence of *H+* and *OH⁻* denoting equilibrium constant of water ($K_w = 10^{-14}$) is known as shown:

$$\left[H^+ \right] = 10^{-pH} \tag{5}$$

$$K_w = \left[H^+ \right]\left[OH^- \right] \tag{6}$$

The activity coefficient of different components (γ_i) and mean ionic activity coefficient is calculated using Davies equation, considering the maximum limit of ionic strength (I) of *0.2 mol/L* (Davies 1962; Nancollas 1966), as given in Eqs. (7) and (8). Defining the ionisation fraction for Mg^{2+}, NH_4^+ and PO_4^{3-} as $\alpha_{Mg^{2+}}$, $\alpha_{PO_4^{3-}}$ and $\alpha_{NH_4^+}$, the ionisation fraction of the different component concentrations is defined as the quotient of free ion concentration and the total concentration of each chemical component:

$$-Log\gamma_i = AZ_i^2 \left[\frac{I^{1/2}}{1+I^{1/2}} \right] - 0.3I \tag{7}$$

$$\gamma = \left(\gamma_{Mg}\gamma_{NH4}\gamma_{PO4} \right)^{1/3} \tag{8}$$

where:
Z_i = valency of the corresponding elements,
A = DeBye-Hückel constant, *0.493*, *0.499*, *0.509*, *0.519* at *5*, *15*, *25*, and *35°C*.

Solution saturation status was represented by two types of solubility products, including conditional solubility product (P_{cs}) and minimum thermodynamic solubility product (P_{so}). The thermodynamic solubility product (P_{so}) is relateds to the solution properties such as ionisation fraction, activity constant and minimum struvite solubility product, whereas conditional solubility product is related to the total concentration of solution species. Solution of higher value of conditional solubility product as equilibrium solubility product ($P_{cs}>P_{so}$), refers to the super solubility of solution. Equal numerical value of P_{cs} and P_{so} characterize the saturated condition of solution, where as $P_{so}<P_{cs}$ demonstrate the under saturated condition of solution. The negative logarithmic value of minimum struvite solubility product (pK_{so}) value, applied in this thermodynamic modelling, was *13.26* (Ohlinger 1999):

$$P_{so} = \frac{K_{so}}{\alpha_{Mg^{2+}}\gamma_{Mg^{2+}}\alpha_{NH_4^+}\gamma_{NH_4^+}\alpha_{PO_4^{3-}}\gamma_{PO_4^{3-}}} \tag{9}$$

$$P_{cs} = C_{T,Mgm}.C_{T,PO4m}.C_{T,NH4m} \tag{10}$$

Solution thermodynamics property specifies the state of saturation, free ion concentrations, presence of ion complexes and state of precipitation. The precipitation of struvite occurs in supersaturated solution, which takes place particularly due to the influence of pH value of the solution and initial reactant concentration (Al-Khayat and Garside 1990). The process is based on the magnesium ammonium phosphate precipitation by mixing magnesium chloride with ammonium di hydrogen phosphate in the presence of the base. Presence of the base provides the solution

increased free ions of phosphate, Eq. (11), thereby increase supersaturation:

$$PO_4^{3-} \Leftrightarrow HPO_4^{2-} \Leftrightarrow H_2PO_4^- \Leftrightarrow H_3PO_4 \tag{11}$$
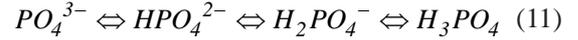
This study incorporated citric acid as a ligand to identify the effect of organic ligand on struvite growth. Citrate forms different chemical complexes with H^+ and Mg^{2+} ions in the active solution. The main thermodynamic equilibria of citrate ion with Mg^{2+} and H^+ are given in Table 2.

Table 2. *Chemical equilibria of citrate in the specified solution*

Equilibrium reaction	*pK value*	*References*
$H^+ + Citrate^{3-} = CitrateH$	*6.33*	*Van der Houwen and Valsami-Jones, 2001*
$2H^+ + Citrate^{3-} = CitrateH^{2-}$	*11.05*	*Van der Houwen and Valsami-Jones, 2001*
$3H^+ + Citrate^{3-} = CitrateH^{3-}$	*14.18*	*Van der Houwen and Valsami-Jones, 2001*
$Mg^{2+} + Citrate^{3-} = MgCitrate$	*3.48*	*Perrin and Dempsey, 1974*

4. STRUVITE GROWTH MODEL

Linear growth rate $\left(\dfrac{dL}{dt} \right)$ of struvite is represented as the function of supersaturation (S), which is demonstrated by Eq. (12) (White 1971; Söhnel and Garside 1992), denoting that K and n are the estimated parameters:

$$G = \frac{dL}{dt} = KS^n \tag{12}$$

In reactor operation struvite crystal grows in a well-mixed vessel in the presence of seeds of size L_0. The newly born crystals diffuse onto the surface of seeds and increase the size to L with lapsed time t. Assuming the mean particle diameter as spherical, the rate of increased volume of a single crystal can be represented by:

$$\frac{dV}{dt} = \frac{d}{dt}\left(\frac{1}{6}\pi L^3 \right) \tag{13}$$

$$\frac{dV}{dt} = \frac{dV}{dL}.\frac{dL}{dt} \tag{14}$$

$$\frac{dV}{dt} = \frac{1}{2}\pi L^2 G \tag{15}$$

Relating to the volume of crystal deposited with mass of crystal, by multiplying the density of the crystal (ρ_c), the rate of mass deposition can be described by:

$$\frac{dm}{dt} = 0.5\pi\rho_c L^2 G \tag{16}$$

For a perfectly mixed struvite reactor, the linear growth rate and mass-deposition rate are

predominantly influenced by supersaturation (concentration gradient), when the temperature remains constant (Tavare 1995):

$$\frac{dL}{dt} = k(C_i - C_0)^n \qquad (17)$$

For struvite Harrison (1999) documented a second-order solution desupersaturation rate (n) along with growth constant (k) as a function of pH. Here the supersaturation based on concentration gradient was the excess concentration of limiting nutrient species (C_i) above the equilibrium solubility concentration (C_0):

$$k = (2.46 \pm 1.24) \times 10^{-5} e^{(1.23 \pm 1.11)(pH - 8)} \quad (18)$$

The linear growth rate, proposed by Harrison (1999), is therefore expressed as a function of pH and concentration gradient:

$$\frac{dL}{dt} = (2.46 \pm 1.24) \times 10^{-5} e^{(1.23 \pm 1.11)(pH - 8)}(C_i - C_0)^2$$
$$(19)$$

A point size distribution of crystal was estimated for the crystal population in which the number of crystals (N) is the function of the mass of seeds (m_0), density of struvite crystal (ρ_c) and initial size of seeds (L_0):

$$N = \frac{m_0}{\frac{\pi}{6} \rho_c L_0^3} \qquad (20)$$

The total rate of mass deposition $\left(\dfrac{dM}{dt} \right)$ can be represented now in the following equation, assuming spherical particles:

$$\frac{dM}{dt} = 0.5 N \pi L^2 A e^{B(pH - C)}(C_i - C_0)^n \qquad (21)$$

A schematic of the modelled process is shown in Figure 1. This system is a fed-batch flow system in terms of the liquid phase and discrete with respect to the solid phase, since it is assumed that all struvite crystals are retained within the reactor. The assumption of perfect mixing enables a simple set of ordinary differential equations to be used to model the dynamics of this system. A point-size distribution is assumed for the crystal population, which, while incorrect, simplifies the modelling of the system. Furthermore, it is assumed that the number of crystals in the reactor is constant, after the system is seeded.
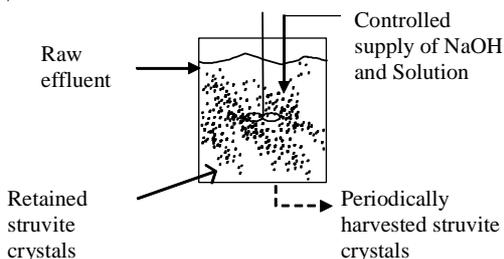

Fig. 1 Schematic of fed-batch struvite reaction system

This model is composed of a set of ordinary differential algebraic equations, based on conservation of mass and sufficient constitutive (thermodynamic and kinetic) relations to uniquely specify the system. Next equation highlighted the fed-batch process model with regard to inlet (F_{in}) reactor flows:

$$\frac{dV}{dt} = F_{in} \qquad (22)$$

The rate of change of solution concentration in the reactor $\left(\dfrac{dC_i}{dt} \right)$ depends on the inlet and outlet flow rates (F_{in}), inlet and outlet concentrations ($C_{i,in}$, C_i), and crystallized struvite mass (M). In fed-batch system of constant composition the rate of de-supersaturation is the same as the total amount of solute in aqueous phase added to the process to maintain stable concentration. Struvite reactor of fed-batch type and constant supplies of solution components are employed to maintain constant composition as well as constant pH. This approach maintains constant supersaturation. However the discrete nature of fed-batch system retain the solution in the reactor so that the outlet concentration (F_{out}) remains zero. Therefore, the mass balance system in fed-batch can be described by:

$$\frac{dC_i}{dt} = F_{in} C_{i,ini} - \frac{dM}{dt} \left(\frac{MW_{c_i}}{MW_s} \right) \qquad (23)$$

The reactor of volume, V, and mass change of the limiting reactant (C_{PO_4}), supersaturation (S) can be symbolized by the next equation if equilibrium concentration (C_{PO_4e}) is known using solution thermodynamic solubility product (P_{so}):

$$S = \frac{C_{PO4}}{V} - C_{PO4e} \qquad (24)$$

To design a struvite process in fed-batch scale, synthetic solution of $NH_4H_2PO_4$ and $MgCl_2$ are used as the source of NH_4, PO_4 and Mg into the reactor. The proposed model was adapted with the $NaOH$ equilibria for pH adjustment to the required level. The synthetic source of NH_4^+ and PO_4^{3-} ($NH_4H_2PO_4$) and synthetic Mg^{2+} source liberated $2M$ of H^+ for each mole of reactants. With known concentration (C_{NaOH}) and operation time in fed-batch system the flow of $NaOH$ (F_{NaOH}) to be added, can be quantified by a simple numerical relation followed by simple chemical equation:

$$NH_4H_2PO_4 + Mg^{2+} \Rightarrow MgNH_4PO_4 + 2H^+ \quad (25)$$
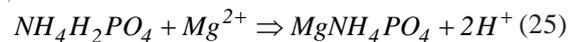
$$2 \left(\frac{dm/dt}{MW_{MAP}} \right) 1000 + F_i.H_{Fi} - F_{NaOH}.C_{NaOH} = 0 \quad (26)$$

5. MODEL RESPONSE AND DISCUSSION

This model was simulated at three different concentrations of citric acid, i.e. *0.0, 0.01* and *0.05 M*, as demonstrated in Figure 2a. The input molar concentration of solution was *0.01 M* for *Mg*, *NH$_4$* and *PO$_4$*, respectively, for the struvite reactor of maximum operating volume *40-L* and initial operating volume of *10-L*. The input mass of seeds in this model was *50*-g of diameter *30-μm*. The model input *NaOH* concentration was *0.25 M* to maintain a constant level of pH of *8.5*. Model response demonstrated in Figure 2b illustrated that mass deposition of struvite is inversely related to citric acid concentration. A higher concentration of citric acid inflicted more inhibition on struvite mass deposition due to complex formation of citrate and metal ion (*Mg^{2+}* ion). Due to the presence of Magnesium Citrate (*MgC*) complex, the free ion concentration was reduced extensively leading to slow chemical reaction among the struvite components in solution. Citrate inhibiting Hydroxyapatite (HAP) and Potassium Ammonium Phosphate (KAP) was

documented in literature using experimental observations (van der Houwen and Valsami-Jones 2001; Srinivasan et al. 1999 and 2002), which was confirmed by the corresponding researcher as the metal complexation effect with organic ligand. A thermodynamic computational approach along with kinetics, in this study, established the inhibiting effect of organic ligand (citrate in this study) on struvite precipitation more rigorously.

Figure 3a described the free ion concentration of magnesium. It is worthwhile pointing out that graphical presentation, on the left side *Y*-axis, corresponds to free magnesium ion concentration with labeled citric acid concentration as mentioned in the bottom legends on the Figure 3a. The extensive reduction of free magnesium ion was observed due to magnesium citrate complex formation, which was inversely related to citric acid concentration (Figure 3a). Figure 2a also demonstrated that concentration of free phosphate ion concentration is directly proportional to the citric acid concentration, since most of the magnesium ion forms complex with citrate and there was less possibility of

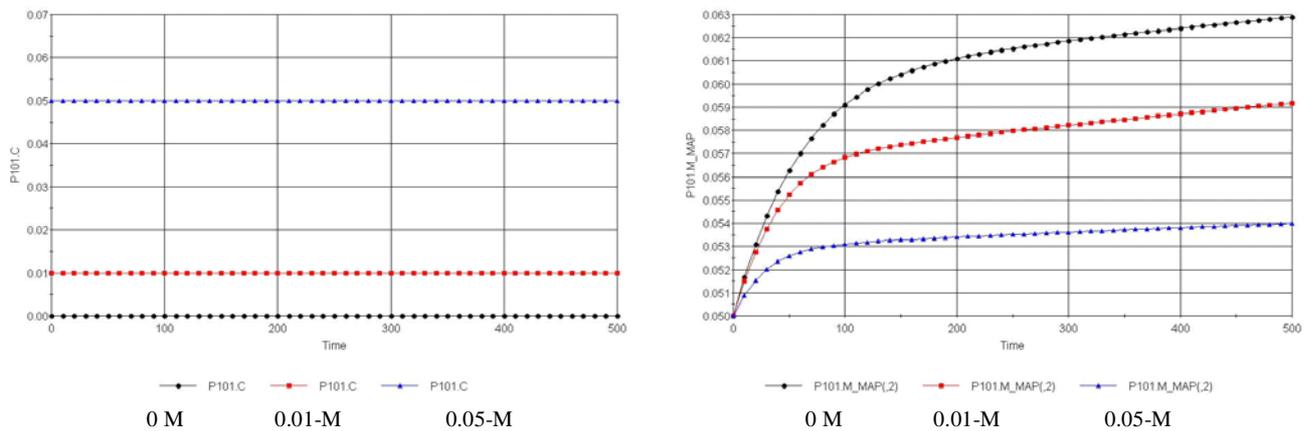| 0 M | 0.01-M | 0.05-M | | 0 M | 0.01-M | 0.05-M |

Fig. 2 (a) Concentration of citrate in the solution as model input parameters with labelled molar concentration; (b) Model response of struvite mass deposition rate at different concentration of citric acid.
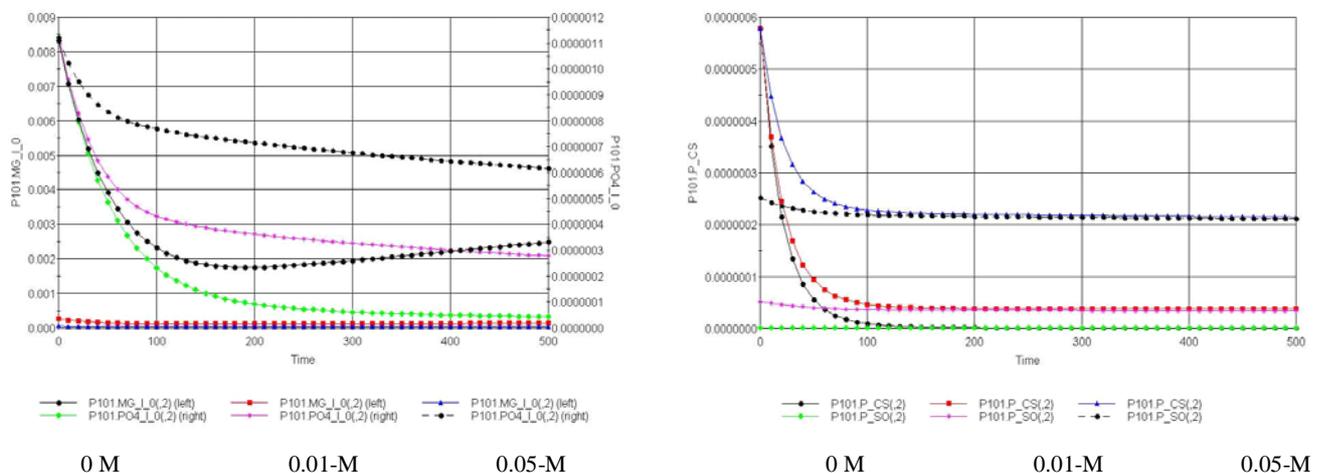

| 0 M | 0.01-M | 0.05-M | | 0 M | 0.01-M | 0.05-M |

Fig. 3 (a) Model response of free Mg^{2+} and PO$_4^{3-}$ at different citric acid concentration; (b) Comparison of conditional solubility product (P$_{cs}$) and thermodynamic solubility product (P$_{so}$) at different citric acid concentration as labelled below the legend in each figure

forming other complexes such as $MgOH^-$, MgH_2PO_4+, $MgHPO_4$, $MgPO_4$, H_3PO_4, $H_2PO_4^-$, PO_4^{3-}, $MgHPO_4$, $MgPO_4^-$. Thus free PO_4^{3-} concentration increases in the presence of citric acid. It is worthwhile pointing out that the free phosphate ion concentration in Figure 3a is represented by the graph in right hand side *Y*-axis. The same type of profile, as free Mg^{2+}, was also observed in model response for free NH^{4+} ion concentration. Due to this complex chemical behavior for citric acid, presence in solution, the conditional solubility product (P_{cs}) and thermodynamic solubility product (P_{so}) of struvite changed significantly.

Figure 4a described the concentration of magnesium citrate complex at different concentration of citric acid while input magnesium concentration of *0.01-M* as model input. It was observed that the concentration of magnesium citrate complex formation depends on the citric acid concentration and they are directly related. Hence, higher concentration of citric acid caused more magnesium citrate complex, which reduced the free Mg^{2+} concentration. It is also remarkable that most of the remaining total magnesium remains in complex form with citrate. As demonstrated in Figure 4a, for the input magnesium and citric acid concentration of *0.01-M* the concentration of *MgC* complex was more than *0.008-M*. The flow rate profile of *NaOH* addition to maintain constant operating pH of *8.5*, at different citrate concentration, is demonstrated in Figure 4b. It was observed that higher citric acid concentration reduced the required flow rate of *NaOH*. It is worthwhile pointing out that stoichiometrically *NaOH* addition rate represents the intensity of struvite formation reaction. Slower *NaOH* addition rate represents the less intense struvite crystallization.

The activity constant for each component, determined using Deby-Huckel equation, depends on concentration. The activity constant of magnesium greatly was reduced with the increase of citrate (Figure 5b). The quotient of struvite mass with total mass in the reactor was also affected inversely with citric acid concentration (Figure 5a).
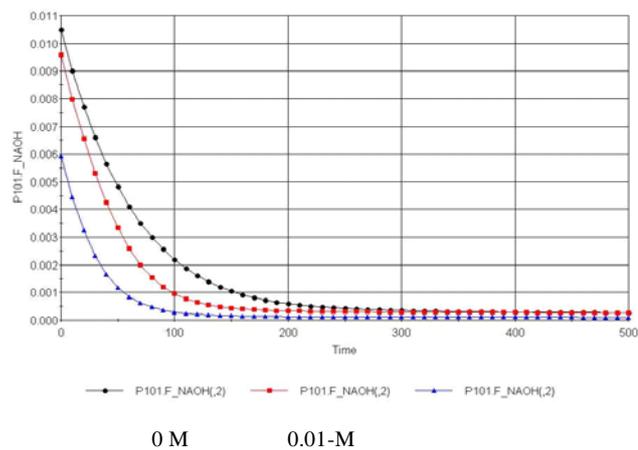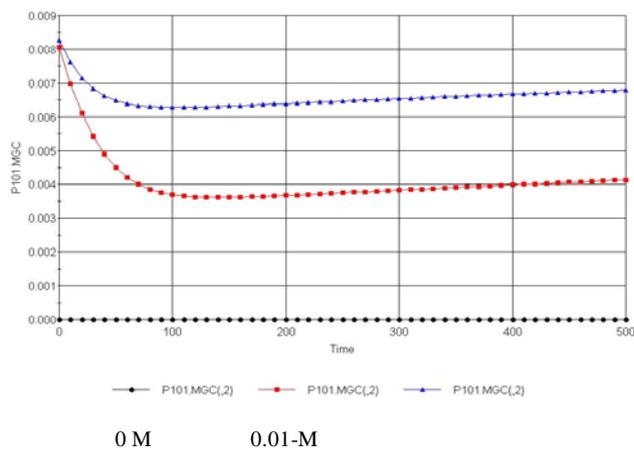

0 M   0.01-M   0 M   0.01-M

Fig. 4 (a) Model response of the magnesium citrate concentration at different citric acid concentration as labelled; (b) Required flow-rate of NaOH to maintain constant pH of 8.5 in the reactor (concentration of citrate is labelled below the legends in each figure).

0 M   0.01-M   0.05-M   0 M   0.01-M   0.05-M
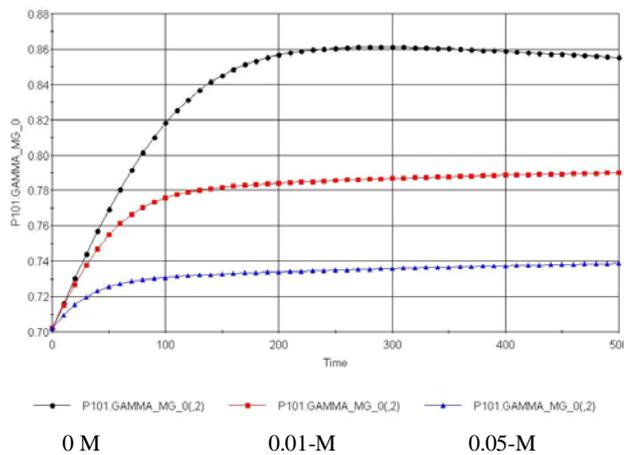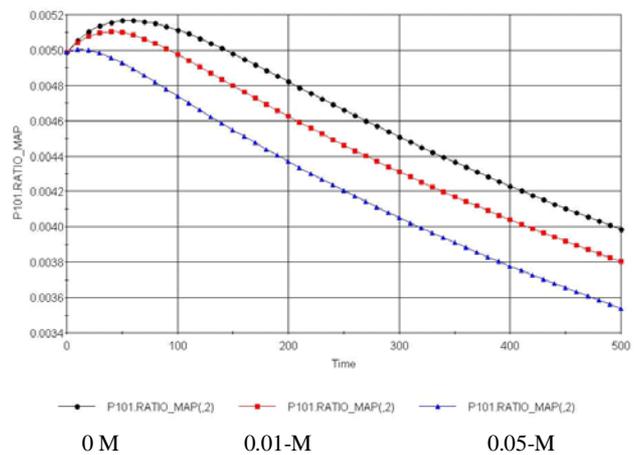
Fig. 5 (a) Mass deposition quotient with total mass in the reactor at different citric acid concentration; (b) Activity constant of magnesium in the solution of different citric acid concentration as labelled below the legends

6. CONCLUSION

It is concluded from the modelling approach that struvite crystallization is inhibited by organic ligand. Chemical equilibria of citrate were included in this modelling, along with chemical thermodynamic and kinetics of struvite. The mass deposition rate was inhibited in the presence of citrate (an organic ligand) due to the complex formation between citrate and magnesium, which reduces the available free Mg^{2+} changing the standard thermodynamic property of solution.

7. REFERENCES

[1] A. Al-Khayat and J. Garside, Calcium carbonate precipitation: The role and importance of solution chemistry, Proc. of the 11th International Symposium of Industrial Crystallization, Garmisch-Partenkirchen, 1990.

[2] C.C. Bouropoulos and P.G. Koutsoukos, Spontaneous precipitation of struvite from aqueous solutions, *Journal of Crystal Growth*, Vol. 213, pp. 381-388, 2000.

[3] C.W. Childs, A spontaneous study of equilibria in aqueous divalent metal orthophosphate solutions, *Inorganic Chemistry*, Vol. 9, No. 11, pp. 2465-2469, 1970.

[4] C.W. Davies, *Ion Association*, Washington, Butterworth, 1962.

[5] E.A. Martell and J.C. Smith, *Critical Stability Constants*, 1989.

[6] E.T. White, *Industrial Crystallization: A Short Course*, University of Queensland, 1971.

[7] F.M. Morel and J.G. Hering, *Principles and Applications of Aquatic Chemistry*, John Wiley and Sons Inc, New York, 1993.

[8] G.H. Nancollas, *Interactions in Electrolytic Solutions*, Amsterdam, 1966.

[9] J.W. Mullin, *Crystallization*, Butterworth-Heinemann Publications, Ipswich, 1993.

[10] K.N. Ohlinger, Kinetics effects on preferential struvite accumulation in wastewater, PhD Thesis, School of Science and Engineering, California State University, 1999.

[11] K.N. Ohlinger, T. M. Young and R.D. Schroeder, Post-digestion using a fluidized bed rector, *Journal of Environmental Engineering*, pp. 261-268, 2000.

[12] M. Harrison, Source reduction of nutrients from abattoir wastewater by struvite crystallization, PhD thesis, Department of Chemical Engineering, University of Queensland, 1999.

[13] N.O. Nelson, R. Mikkelson and D. Hesterberg, Struvite precipitation in anaerobic swine lagoon: Effect of pH and Mg:P ration and determination of rate constant, *Biosource Technology*, Vol. 89, pp. 229-236, 2003.

[14] N.R. Nelson, R.L. Mikkelson and D.L. Hesterberg, Struvite formation to remove phosphorus from anaerobic swine lagoon, Proc. of the 8th International Symposium on Animal, Agriculture and Food Processing Wastes, Des Moines, pp. 18-26, 2000.

[15] P.R. Battistoni, D. Boccadoro, D. Bolzonella and S. Pezzoli, Optimization of chemical and physical pretreatment in a platform for the treatment of liquid industrial wastes, *Industrial Engineering Chemical Research*, Vol. 40, pp. 4506-4512, 2001.

[16] S.N. Tavare, *Industrial Crystallization: Process Simulation Analysis and Design*, New York and London, Plenum Press, 1995.

OPSEŽAN RAČUNALNI PRISTUP S CILJEM DA SE PREPOZNA DJELOVANJE LIGANADA NA KRISTALIZACIJU STRUVITA

SAŽETAK

Rad se bavi prvenstveno projektom procesa struvita i bazira se na rješenju pomoću termodinamike i kinetike. Struvit je kristal čiji je kemijski sastav $MgNH_4PO_4 \cdot 6H_2O$. Dominantni parametri u termodinamici su termodinamičke ravnoteže i pH vrijednost. Glavno rješenje u kemiji su složene tvorbe (spojevi) između Mg, NH_4 i PO_4 koje uključuju Mg^{2+}, $MgOH^-$, $MgH_2PO_4^+$, $MgHPO_4$, $MgPO_4$, H_3PO_4, $H_2PO_4^-$, PO_4^{3-}, $MgHPO_4$, $MgPO_4^-$, NH_3. Kinetički parametri uključeni u ovo modeliranje su taloženje mase, veličina rastućeg kristala itd. Modeliranje se provodilo u serijskoj računalnoj obradi. Rad se usredotočio na uključivanje termodinamičkih ravnoteža da bi se prepoznalo djelovanje liganada na rast struvita, te na kinetičko i kemijsko rješenje. Modeliranje je uzelo citrat kao ligand. Simulacijski se pristup obavio pomoću simulacijskog proces paketa gPROMS.

Ključne riječi: struviti, proces, modeliranje, simulacija, serijska računalna obrada, ligandi.