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Model-driven experimental evaluation of struvite nucleation, growth and aggregation kinetics

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ABSTRACT

Nutrient stewardship is emerging as an issue of global importance, which will drive the development of nutrient recovery in the near to medium future. This will impact wastewater treatment practices, environmental protection, sustainable agriculture and global food security. A modelling framework for precipitation-based nutrient recovery systems has been developed, incorporating non-ideal solution thermodynamics, a dynamic mass balance and a dynamic population balance to track the development of the precipitating particles. The mechanisms of crystal nucleation and growth and, importantly, aggregation are considered. A novel approach to the population balance embeds the nucleation rate into the model, enabling direct regression of its kinetic parameters. The case study chosen for the modelling framework is that of struvite precipitation, given its wide interest and commercial promise as one possible nutrient recovery pathway. Power law kinetic parameters for nucleation, crystal growth and particle aggregation rates were regressed from an ensemble data set generated from 14 laboratory seeded batch experiments using synthetic solutions. These experiments were highly repeatable, giving confidence to the regressed parameter values. The model successfully describes the dynamic responses of solution pH, the evolving particle size distribution subject to nucleation, growth and aggregation effects and the aqueous magnesium concentration in the liquid phase. The proposed modelling framework could well be extended to other, more complex systems, leading to an improved understanding and commensurately greater confidence in the design, operation and optimisation of large-scale nutrient recovery processes from complex effluents.

1. Introduction

The development of nutrient recovery systems, focussing on phosphorus, will play a key role in assuring future global food security. Phosphorus for fertiliser production is currently sourced by mining phosphate rock. Unabated, the consequence of continued mining will be a peak in phosphorus production, expected to be reached by the middle of this century. This will lead to increasing fertilizer prices, making food more expensive (Cordell et al., 2009).

The present work develops a framework for modelling nutrient recovery processes, using struvite precipitation as a case study, given its potential importance to global nutrient recovery (Driver et al., 1999; Maurer et al., 2006; Udert et al.,

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2003). While other nutrient recovery pathways exist, struvite is the most widely studied (Le Corre et al., 2009) and has already been commercially applied (Ostara Nutrient Recovery Technologies Inc., Multiform Harvest Inc. and Nutrients Recovery Systems BVBA).

Struvite forms according to the stoichiometry in Equation (1).

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightleftharpoons MgNH_4PO_4 \cdot 6H_2O_{(s)} \quad (1)$$

Previous studies have concentrated on understanding the thermodynamics of struvite formation and the application of different reactor configurations (Adnan et al., 2003b; Ali and Schneider, 2006; Doyle and Parsons, 2002; Jaffer et al., 2002; Mavinic et al., 2007; Ohlinger et al., 1998; Ronteltap et al., 2007, 2010; Von Münch and Barr, 2001). Modelling the process fundamentals, with a particular focus on nucleation, crystal growth and particle aggregation, promises to strengthen the application of nutrient recovery technologies, since their design, operation and optimisation would be better understood. As such, the kinetics of the struvite precipitation process must first be quantified to formulate any process model. To date this has been lacking in the scientific literature.

While acknowledging the range of possible particle mechanisms, most struvite kinetic studies to date have been limited to crystal growth and, occasionally, nucleation phenomena (Ali and Schneider, 2008; Bhuiyan et al., 2008; Hanhoun et al., 2013; Harrison et al., 2011; Mehta and Batstone, 2013; Triger et al., 2012), or they ignored particle formation/growth mechanisms altogether (Borja et al., 2008; Le Corre et al., 2007b; Nelson et al., 2003; Quintana et al., 2005; Turker and Celen, 2007). Ideally, a more general modelling approach would construct a population balance that incorporates the key mechanisms involved with struvite precipitation: nucleation, crystal growth and aggregation. While population balances have been used by Triger et al. (2012) and Hanhoun et al. (2013), they only considered nucleation and crystal growth, neglecting aggregation without adequate justification.

One detailed study on struvite aggregation has been performed, it focused on the addition of coagulants and their efficacy (Le Corre et al., 2007a). Their suggestion that aggregation without the addition of coagulants is not significant in the case of struvite (Le Corre et al., 2007a) was used as the basis to neglect aggregation altogether in further studies (Hanhoun et al., 2013; Triger et al., 2012). However, photomicrographic evidence presented in a number of studies (Adnan et al., 2004; Fattah et al., 2008; Moerman et al., 2009) and the fact that many processes produce aggregated particles desirable for the fertiliser market (Adnan et al., 2003a,b; Britton et al., 2005; Moerman et al., 2009), suggest otherwise. As such, models of nutrient recovery processes must incorporate aggregation to better describe, and therefore design, operate and optimise nutrient recovery systems.

Tracking the dynamics of the size distribution of precipitating particles is carried out using the population balance equation (PBE). The PBE can account for the birth of nuclei from supersaturated solution, the subsequent growth of those nuclei and introduced seed crystals, and the aggregation of particles suspended within the precipitation volume. The population balance equation for a continuous, batch, or fed-batch (depending on the magnitude of the inflows and outflows to the reactor) mixed suspension, mixed product removal crystalliser with negligible volume change including nucleation, size-independent crystal growth and aggregation is given by Equation (2) (Randolph and Larson, 1988).

$$\frac{\partial n}{\partial t} + G\frac{\partial n}{\partial L} = B(L) - D(L) - \sum_k \frac{n_k Q_k}{V} \quad (2)$$

In this equation t is time, L is particle length, $n(t,L)$ is the number density function in the reactor, G is the rate of increase in size of the particles due to crystal growth, $B(L)$ and $D(L)$ are the birth and death functions, respectively, n_k is the number density in (the input or output) stream k and Q_k is the flow rate of stream k and V is the reactor volume. In the system modelled here, the birth and death functions will be determined by the mechanism of the aggregation process; when two particles (of sizes L_1 and L_2) aggregate into a larger particle (size L_3) then the two particles involved in the aggregation event contribute to the death function and the product particle contributes to the birth function. An initial condition $n(L,t=0)$ representing the initial particle size distribution, and a boundary condition $n(L=0,t)$ related to the nucleation rate, are required in order to solve this equation. Analytic solutions for the PBE are available for a few limited cases, requiring assumptions that are invalid for practical systems (Ramkrishna, 2000). Therefore, numerical methods are required to solve the PBE.

Solving a discretised form of the PBE is a common approach, which transforms the continuous partial differential equation into a number of ordinary differential equations, one for each discrete interval of the continuous domain, which can then be solved simultaneously. The interested reader is directed to the cogent discussion on the formulation, advantages and disadvantages of various methods of solution found in Costa et al. (2007).

Hanhoun et al. (2013) used the method of moments to solve the PBE, explained in Randolph and Larson (1988). Disadvantages of the method of moments are that it reduces distributed variables to an average which makes reconstructing the true distribution from its moments numerically unstable (Costa et al., 2007). Furthermore, the first order discretisation used by Triger et al. (2012), results in large errors to the mass balance if the discretisation is not sufficiently fine (Hounslow, 1990) and cannot easily incorporate aggregation processes.

2. Materials and methods

The methodology used combines process modelling with laboratory experimentation. A model describing struvite precipitation incorporating the mechanisms of nucleation, growth and aggregation is developed and executed via computer simulation. For further detail on model development, and potential applications of the model to process design scenarios, the interested reader is referred to Galbraith and Schneider (2014).

A series of experiments yielded an ensemble data set that was subsequently used to regress the model's kinetic parameters for nucleation, crystal growth and aggregation.