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Simultaneous determination of nucleation and crystal growth kinetics of struvite using a thermodynamic modeling approach

Mary Hanhoun\textsuperscript{a}, Ludovic Montastruc\textsuperscript{a}, Catherine Azzaro-Pantel\textsuperscript{a,*,b}, Béatrice Biscans\textsuperscript{a}, Michèle Frêche\textsuperscript{b}, Luc Pibouleau\textsuperscript{a}

\textsuperscript{a} Université de Toulouse, Laboratoire de Génie Chimique, UMR 5503, CNRS/INP/UUPS, BP 84234, INP-ENSIACET, 4 allée Emile Monson, 31030 Toulouse cedex 4, France
\textsuperscript{b} Université de Toulouse, CIRIMAT, UMR 5085, CNRS/INP/UUPS, BP 44362, Campus INP-ENSIACET, 4 allée Emile Monson, 31432 Toulouse cedex 4, France

HIGHLIGHTS

► This work concerns the controlled struvite formation by precipitation.
► We model nucleation and growth kinetics.
► A thermodynamic model is coupled with a population balance.
► The model predicts particle size distribution vs. experimental time.
► It allows the identification of nucleation and particle growth kinetics parameters.

ABSTRACT

This work concerns the controlled struvite formation (MgNH\textsubscript{4}PO\textsubscript{4}·6H\textsubscript{2}O) by precipitation as an alternative removal of phosphorus and, consequently, of ammonium from wastewater discharges. A new method, based on an integrated methodology, is proposed here for predicting and controlling struvite nucleation and growth rate. Experiments were conducted in an isothermal stirred batch reactor at a temperature of 25 °C from a synthetic aqueous solution at different pH levels (8.5−9.6). The initial concentrations of Mg, PO\textsubscript{4} and NH\textsubscript{4} are fixed at 3 mmol/L, then at 4 mmol/L with a molar ratio of Mg/NH\textsubscript{4}/PO\textsubscript{4} equal to 1. Crystal size is determined by laser granulometry and morphometry. A population balance-based model coupled with a thermodynamic model predicts particle size distribution vs. experimental time using a reconstruction model. This approach is particularly numerically stable for the identification of nucleation and particle growth kinetics parameters that are used to predict crystal size distribution. The methodology is based on a thermodynamic model previously developed for which pH control and supersaturation constitute key parameters. The obtained results are of major importance for the design of struvite precipitation reactor, and for the development of crystal growth control methodology.

Keywords: Struvite, Precipitation, Modeling, p-Recovery, Nucleation−growth, Population balance, Stirred reactor

1. Introduction

The cost of environmental protection and pollution prevention is increasing above all because of stringent effluent quality standards. In this context, phosphate impact on water pollution plays a major role since it promotes eutrophication. One proposed solution to this problem is the recovery of phosphate using crystallization. This work addresses the problem of phosphorus recovery from synthetic wastewater by precipitation of struvite. The general objective is to develop a methodology for optimal design of an automated pilot reactor for wastewater treatment.

Two major crystallization processes have been developed for phosphorus recovery from wastewater, respectively the so-called calcium phosphate (CP) precipitation process and the magnesium ammonium phosphate (MAP) or struvite precipitation which is a crystalline substance consisting of magnesium, ammonium and phosphorus in equal molar concentrations (MgNH\textsubscript{4}PO\textsubscript{4}·6H\textsubscript{2}O). Struvite forms according to the following reaction [1]:

\[
\text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} + 6\text{H}_2\text{O} \rightarrow \text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}
\]  

(1)

It is important to understand and optimize the precipitation process in order to improve product quality, thus minimizing the associated production costs. A previous study [2−5] based on a thermodynamic model was developed to predict the quantity of
precipitated product under the form of struvite and to determine
the evolution of supersaturation and pH with time. Even if conver-
sion rate is an important parameter to control process efficiency, it
must be emphasized that crystal size distribution is a key element
to control product quality.

Previous studies have shown an influence of pH, mixing energy
and solution type on struvite growth rate [1,2,7,30,31]. However,
these studies take into account the mean particle size rather than
particle size distribution. The purpose of this study is to evaluate
nucleation and growth kinetics laws, using a population balance,
and to compare modeling results with experimental particle size
distribution.

This paper is organized into four sections.

As mentioned in Section 1 of this paper, the purpose of this
study is to develop a methodology to predict particle size distri-
bution. One-dimensional growth modeling in a batch reactor based
on nucleation–growth crystal formation is investigated and pre-
presented in Section 2. The nucleation model is based on a classical
logarithmic formulation proposed by [10,11] depending on super-
saturation. The growth model is based on a variable order of super-
saturation. In parallel, preliminary experiments were carried out at
different initial supersaturation values to determine the induction
time and to identify the involved nucleation phenomenon, as well
as to evaluate the final particle size distribution in a stirred reactor.
Section 3 proposes an innovative strategy based on the classical
method of moment [5] to compute nucleation and growth param-
eters. The major interest of this strategy is to combine a previous
developed thermodynamic model [4] and a population balance-
oriented one for a more robust determination of these parameters.
An optimization procedure was thus carried out, that is based on
the minimization of the discrepancy between the experimental
 supersaturation and the value predicted by the thermodynamic
model so as to determine the nucleation and growth parameters.
Section 4 is devoted to the identification of nucleation and particle
growth kinetics parameters, using the methodology described in
Section 3. They are then used to predict the size distribution that
is typical of a nucleation–growth model by a reconstruction meth-
ood [7]. Finally, Section 5 concludes this work and gives some
guidelines for struvite precipitation reactor design.

2. General modeling framework

2.1. Coupling a thermodynamic model with a nucleation–growth
model

The proposed framework (see Fig. 1) involves a two-step mod-
eling approach. The first step is based on an equilibrium prediction
of the studied system Mg₃PO₄·NH₄Cl that was developed in a previ-
ous work [4]. This model computes the final conversion rate of
phosphate (X) as a function of equilibrium pH for different tempera-
tures and supersaturations. From the experimental evolution of
pH and the initial concentrations, the model gives the evolution of
 supersaturation vs. time. This is the starting point for the evalu-
ation of growth and nucleation rates during the second step of the
methodology.

The numerical strategy implies a genetic algorithm (NSGA II) [8]
both to initialize a classical algorithm of resolution (involving a
classical Newton–Raphson method) and to guarantee the robust-
ness of the process. This model requires as inputs the initial
concentrations of phosphate, ammonium and magnesium in
wastewater, temperature as well as the quantity of sodium
hydroxide that is initially added. The phosphate conversion rate
X is discretized in the interval bounded by zero and the final con-
version rate as upper limit, which then allows the identification of
 supersaturation with time. Major results are reported in [4]. A
second modeling step, which is the core of this investigation in-
volves the development of a nucleation–growth model based on
a population balance to predict the kinetic parameters of nucle-
ation and crystal growth of struvite as well as the particle size dis-
tribution using the previous developed thermodynamic model.

2.2. Principles of population balance-based modeling

2.2.1. Formulation of population balance equation

This work involves the development of a model of nucleation
and growth in a batch reactor. The formalism of the population bal-
ance equation to describe the evolution of the crystal size distri-
bution during the size in a process of crystallization [9] assumes that
neither agglomeration nor breakage occurs and that the expression
of growth rate is independent of crystal size. Nucleation rates im-
ply that several phenomena such as homogeneous and heteroge-
nous nucleation need to be taken into account. The secondary
nucleation characterization depends on the degree of mixing in a
stirred reactor. The experiments were carried out in a batch reactor
with a rotational speed of around 500 rpm at 25 °C. Under these
conditions, only primary nucleation occurs with the presence of
fines and the crystals grow without agglomeration (no breakage).

\[
\frac{\partial n(t, L)}{\partial t} = -G(t, m) \frac{\partial n(t, L)}{\partial L} + r_n(t, m) \times \delta(L - L_0)
\]

(2)

\[
n(t = 0, L = 0^+) = 1 \quad \text{and} \quad n(t = 0, L = 0) = 0
\]

In this expression, \(m = m(t) > 0\) represents the solute mass in the
liquid phase, \(n_0(L)\) represents the initial crystal size distribution.
\(G(t, m)\) is the crystal growth rate that is independent of crystal size;
\(r_n\) corresponds to the crystal nucleation rate for a minimal size \(L_0\).
\(\delta\) is the Dirac function representing the spontaneous appearance
of crystals.

According to the theory of nucleation and growth [10,11], nuclea-
 tion rate \(r_n\) that represents the number of struvite nuclei formed by
time unit (s) and volume unit (cm³) follows the general equation:

\[
r_n = \alpha \times \exp \left( -\frac{R}{\ln \Omega^*} \right) \quad \text{Particle m}^{-3} \text{s}^{-1}
\]

(3)

The kinetics of crystal growth is expressed by:

\[
G = kg a^3 \quad (\text{ms}^{-1})
\]

(4)

where \(A, B, kg,\) and \(g\) are the kinetic parameters to be identified.
\(\Omega^*\) is the supersaturation ratio as expressed by:

\[
\Omega^* = \left( 1 - \frac{a_{IO} - a_{IO}^*}{K_{sp}} \right)^{1/3}
\]

(5)
aᵢ represents the ionic activity of species \(i\) related to struvite in the
solution. \(K_{sp}\) is struvite solubility product, which was determined
equal to \(10^{-13.17}\) (mol/L)³ at 25 °C in [4].

In general, the population balance involves differential equa-
tions to model the population density distribution. Many examples
such as [12,9,13–16] can be found. Analytical solutions of the popu-
lation balance equation can be obtained only for simple cases. Yet,
a numerical solution is required in the majority of cases.

In that context, the method of moments is one of the simplest
techniques for solving the population balance equation. It
translates the population balance equation into a set of ordinary
differential equations in terms of moments of size distribution. It
makes it possible to use the experimental crystal size distributions
directly with a good compromise between precision and speed of
resolution. This method was chosen here to develop a model of
nucleation–growth of struvite in a perfectly stirred reactor starting
from a population balance equation under the assumption that
neither agglomeration nor breakage occurs. It must be emphasized
that no agglomeration was mentioned in the work of [17] which is in agreement with the assumption that is considered here: struvite has negative potential zeta in the range of pH (8.5–10.5). It must be highlighted that some crystal samples were collected along batch evolution and do not exhibit the presence of dust (fines) or broken crystals.

Since the condition of supersaturation is verified here, nucleation (or germination) can occur. The nuclei (or germs) are the smallest crystals that are thermodynamically stable. To understand the nucleation process, it is thus necessary to investigate the kinetic mechanisms leading to the formation of nuclei. The terminology suggested by Mullin [10] is adopted in this work. The involved mechanisms depend on the explored operating conditions during nucleation and on the physicochemical properties of the medium. Primary nucleation concerns the formation of the new solid phase that occurs in systems that do not contain previously crystalline materials. Two types of primary nucleation are generally distinguished: (i) homogeneous primary nucleation for which the new solid phase appears starting from a supersaturated solution that is free from any impurity; and (ii) heterogeneous primary nucleation for which the formation of the new solid phase is catalyzed by the presence of some impurities in the solution.

In most cases [10], as in this work, nucleation cannot be homogeneous (primary) and nucleation is initiated either by suspended particles or by the walls of the reactor.

In some specific cases, the phenomena of nucleation are preceded by the so-called induction time.

2.2.2. Population balance resolution by the method of the moments

Eq. (2) cannot be solved analytically. The population balance can be transformed by the method of moments by writing the kth-order moment noted $\mu_k$, as follows:

$$\mu_k(t) = \int_0^\infty L^k n(t, L) dL$$  \hspace{1cm} (6)

The moments are computational tools leading to the characteristics of particle sizes

$$\mu_0 = \int_0^\infty n(L) dL = NT$$  \hspace{1cm} (7)

In this expression, $N_t$ represents the total number of particles. To determine the particle size distribution number, the evolution of the 0th-order moment is thus required.

$$\mu_1 = \int_0^\infty L \times n(L) dL = L_1 = \phi_1 \frac{\mu_1}{\mu_0}$$  \hspace{1cm} (8)

$L_1$ indicates the mean particle size and $\phi_1$ is the size shape factor ($\phi_1$ = 1 in the case of spheres);

$$\mu_2 = \int_0^\infty L^2 \times n(L) dL = A_1 = \phi_2 \frac{\mu_2}{\mu_0}$$  \hspace{1cm} (9)

$A_1$ is the average surface of the particles and $\phi_2$ is the shape factor of form ($\phi_2 = 4$ in the case of sphere);

$$\mu_3 = \int_0^\infty L^3 \times n(L) dL = V_1 = \phi_3 \frac{\mu_3}{\mu_0}$$  \hspace{1cm} (10)

$V_1$ indicates the volume average particle volume and $\phi_3$ is the volume shape factor ($\phi_3 = 1/6$ in the case of sphere).

According to [18], the mass balance in the liquid phase can be expressed as follows:

$$\frac{dm(t)}{dt} = -3 \rho_c \phi_v G(t, m) \times \mu_2(t)$$  \hspace{1cm} (11)

where $\rho_c$ is the crystal density, $\phi_v$ is the volume shape factor. SEM imagery makes it possible to observe the formed crystal shape. The shape factor is fixed at 0.01 to take into account the needle form, as proposed in [6] and confirmed by our observations (see Fig. 8). Kinetics values are of course related to the assumptions made for the shape factor value.

By using the definition of the moments (Eq. (6)), the population balance Eq. (2) and the mass balance (11), a system of ordinary differential equations [6,19–24] is obtained:

$$\frac{dN_t(t)}{dt} = r_n(t, m)$$  \hspace{1cm} (12)

$$\frac{d\mu_2(t)}{dt} = i \times G(t, m) \times \mu_{k-1}(t)$$  \hspace{1cm} (13)

$$m(t) + \rho_c \phi_v \mu_2(t) = m(t_0) + \rho_c \phi_v \mu_2(t_0)$$  \hspace{1cm} (14)
The initial values of the moment and the solute mass are positive:

\[ \mu_i(t_0) > 0, \quad m(t_0) > 0, \quad i = 0, 1, 2, 3 \]

The mass of the formed crystal is not usually used in the field of crystallization. It is thus necessary to express the distribution size number as a function of the number of crystal moles that are formed under conditions of supersaturation. Then, the laws of growth and nucleation are written according to the medium supersaturation. Absolute supersaturation \( S^* = (\alpha_{\text{eq}} - \alpha_{\text{eq}})^{1/3} \) makes it possible to obtain the number of crystal moles per volume unit that can be formed at equilibrium state. The use of supersaturation in the material balance implies that the equilibrium is achieved at date \( t \). By dividing the mass balance Eq. (14) by the molar mass \( M_i \) of the formed crystal, the following expression is then obtained:

\[ s(t) + \frac{\rho_i \phi_i}{M_i} \mu_i(t) = s(t_0) + \frac{\rho_i \phi_i}{M_i} \mu_i(t_0) \tag{15} \]

The resolution of the resulting ordinary differential equation system (Eqs. (12) and (13)) allows the computation of the evolution of the 3rd order moment \( \mu_3 \) vs. time. Eq. (15) leads to the evolution of the absolute supersaturation with time.

3. Methodology for determination of nucleation and crystal growth kinetic parameters

The objective of this section is to present how the thermodynamic model that was developed in a previous work can be used to determine the evolution of supersaturation with time from the computation of \( \mu_3 \) and species concentration assuming that a quasi-equilibrium state is reached. Indeed, for initial \( \mu_3 \) and a given wastewater quality, it is possible to compute the phosphorus conversion rate at steady state, and thus, the associated supersaturation and \( \mu_3 \). Briefly, the thermodynamic model developed in [4] allows the computation of the evolution of \( \mu_3 \) vs. time using supersaturation.

The kinetic constants of nucleation and growth of struvite can be determined by minimizing the squared difference between the experimental and computed supersaturation values. This method does not require the use of a granulometric analysis, but is sensitive to the accuracy of the thermodynamic model. To our knowledge, this type of approach has not yet been explored in the dedicated literature. The 4th order moment depends on the crystal density number \( \mu_4 \). It is therefore possible to compute this density number by mathematical methods for moment inversion of order \( K \) \( \mu_4 \) (Eq. (6)). The evolution of the absolute supersaturation vs. time is calculated by solving the involved differential equations using the following equation:

\[ s(t) + \frac{\rho_i \phi_i}{M_i} \mu_i(t) = s(t_0) + \frac{\rho_i \phi_i}{M_i} \mu_i(t_0) \tag{16} \]

The methodology is explained as follows (see Fig. 2):

- For each experiment (concentration of Mg, NH₄, PO₄ and different pH values), the relative supersaturation \( S = s/\mu_4 \) is the absolute supersaturation, \( s = (\alpha_{\text{eq}} - \alpha_{\text{eq}})^{1/3} \) is the solubility of struvite, \( \mu_4 = (\alpha_{\text{eq}})^{1/3} \) in the domain of pH variation is calculated. This domain is discretized with a constant step equal to 0.001.
- This step is followed by an interpolation using a polynomial model to obtain a continuous function \( S = f(pH) \).
- Then, the value of supersaturation is computed for the experimental pH value \( S_{\text{exp}} = f(pH_{\text{exp}}) \) using the function \( S = f(pH) \).

The experimental supersaturation vs. time \( S_{\text{exp}} = f(t) \) is finally obtained.

The determination of the parameters \( A, B, \) and \( g \) using experimental data is carried out by minimizing the quadratic function as follows:

\[ \min[F(A, B, g)] \]

With

\[ F(A, B, g) = \sum_{t=1}^{n} \sum_{t=1}^{n_{exp}} \left[ S_{\text{model}}(t) - S_{\text{exp}}(t) \right]^2 \tag{17} \]

\( n_{exp} \) is the number of experiments, \( t \) the time corresponding to an experimental point, \( \tau_{\text{end}} \) the time at the end of an experiment, and \( S \) the relative supersaturation obtained by the resolution of the set of differential equations: experimental relative supersaturation is calculated by the thermodynamic model for initial concentrations of \( \text{[Mg], [PO}_4, \text{[NH}_4] \) and \( \text{pH} \) at time \( t \).

The resolution of the abovementioned optimization problem gives the kinetic parameters of nucleation and growth rate values for struvite. Since the problem belongs to the class of nonlinear optimization, it is necessary at first time to explore a large space because many local minima may exist. Then, a growth rate expression that is valid for all the experiments is identified. Finally, the experimental crystal size distribution is compared with the computed ones by use of the method of reconstruction of the crystal size distribution, as explained in the Electronic annex (reconstruction of crystal size distribution section).

4. Experimental determination of nucleation and crystal growth kinetic parameters

4.1. Induction time

The induction time corresponds to the time between the establishment of supersaturation and the occurrence of first nuclei. It depends directly on the degree of supersaturation, temperature and the presence of impurities in the solution. Its experimental measurement is not straightforward and depends strongly on the sensitivity of the sensor, that is to say a pH-meter [1], turbidimeter [25], absorption measurement [26]. According to [27], the induction time is inversely proportional to nucleation rate (either homogeneous or heterogeneous).

\[ t_{\text{ind}} = \frac{1}{R(A)} \tag{31} \]

When combining Eqs. (3) and (31) and applying the log transformation, we obtained the following equation:

\[ \ln(t_{\text{ind}}) = \ln(R(A)) = - \ln(A) \tag{32} \]

The parameter \( B \) is described in Eq. (3) and \( A \) is a function of parameter \( A \) (Eq. (3)).

The induction time can be observed through experiments, between the beginning of an experiment and the beginning of variation of solution pH, which corresponds to the beginning of crystal growth and the end of the induction period. The value of \( t_{\text{ind}} \) allows a direct determination of the values of the kinetic parameters both for homogeneous or heterogeneous nucleation.

4.2. Experimental determination of the nucleation rate constant

Experiments were carried out at different initial supersaturation values in a stirred reactor (3L) at a rotational speed of around 500 rpm with 25 °C. Stock solutions of magnesium and ammonium phosphate were prepared from corresponding crystalline solids, i.e., MgCl₂·6H₂O and NH₄H₂PO₄. Deionised water was used to prepare the synthetic wastewater solution. The supersaturated
solutions (corresponding to a final phosphorus concentration of respectively 3 and 4 mmol/L) with a Mg/NH$_4$/PO$_4$ molar ratio equal to 1 were prepared by rapid mixing of NH$_4$H$_2$PO$_4$ 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. The reaction is studied in supersaturation range $1.83 < \Omega < 3.44$. The initial concentrations of Mg, PO$_4$ and NH$_4$ were fixed at 3 mmol/L, then at 4 mmol/L, with variable initial pH comprised between 8.5 and 9.5 and with an Mg/NH$_4$/PO$_4$ molar ratio equal to 1. Each experimental point is repeated three times for guaranteeing repeatability, and these three values are inserted in the computation for identification. The experimental points are available in the Electronic annex.

The induction times were defined as being the duration starting from the initial mixture of the solutions until the first change of pH corresponding to the beginning of precipitation, for this reason, the pH is selected as the indicator of precipitation. The mixing time (6.6 s) is not negligible as compared to the induction time in the case of homogeneous nucleation. The lowest value of the induction time is about 15 s, which corresponds to both mixing and induction time. This is why the parameter $B$ obtained from the experiments i.e., 9.93 (respectively 0.9) for homogeneous (respectively heterogeneous) nucleation is only used to have an order of magnitude to calculate the parameters of nucleation and growth rate of struvite.

In Fig. 3, two zones can be observed, corresponding to both mechanisms of primary nucleation that are homogeneous and heterogeneous. The transition between homogeneous and heterogeneous occurs at a value of $-\frac{1}{\ln \Omega}$ equal to 0.96, which leads to a supersaturation ratio $\Omega$ lower than 2.68.

The value of the parameter $B$ determined during this study (Fig. 3) is used to check the order of magnitude of this parameter. The next stage concerns the determination of struvite crystal growth rate.

4.3. Variation domain of the parameters for nucleation and crystal growth

The optimization of nucleation and growth rate parameters requires the determination of the variation domain of these parameters. Let us recall that the objective is to find the parameters allowing at the same time to have an evolution according to the time of relative supersaturation that is in agreement with the experimental profile.

A value of $A$ equal to $10^{22}$ m$^3$ s$^{-1}$ is proposed in the literature [28] without yet specifying the conditions under which this value is given. During some preliminary tests, by taking this value as a reference, the results were very far from the experimental ones. A sensitivity analysis for these parameters was thus performed.

The following strategy was implemented:

- The value of the parameter $g$ is fixed at 2 (when growth is controlled by integration, the value of $g$ is comprised between 1 and 2).
- The value of parameter $A$ is changed "manually" between $10^6$ and $10^{12}$.

Then, the parameters $B$ and $k_g$ are given so that the relative supersaturation vs. time as predicted by the model takes the nearest possible value of the experimental ones (cf. Fig. 2). Figs. 4 and 5 present the variations of parameters $A$, $B$ and $k_g$ for homogeneous and heterogeneous nucleation. From this basis, the parameter range can be determined:

- Parameter $A$: the maximum crystal size obtained in the experimental runs (SEM observations and morphometry) is about 70 $\mu$m for homogeneous nucleation and reaches 75 $\mu$m for heterogeneous nucleation. It can thus be assumed that parameter $A$ can vary between $10^6$ and $10^{12}$ for homogeneous nucleation (respectively between $10^6$ and $10^9$ for heterogeneous nucleation).
- Parameter $B$: is comprised between 7 and 8 for homogeneous nucleation, (respectively between 0 and 1 for heterogeneous nucleation). These values are confirmed by the induction time values obtained in experimental runs.
- Parameter $k_g$ varies between $10^{-8}$ and $10^{-3}$ m s$^{-1}$ for homogeneous nucleation (respectively between $10^{-6}$ and $10^{-2}$ m s$^{-1}$ for heterogeneous nucleation).

Table 1 shows the variation domains used to optimize these parameters.
4.4. Calculation of the kinetic parameters for homogeneous and heterogeneous nucleation and growth

The determination of the parameters for the general growth rate requires to take into account all the experimental series in the optimization phase and also to distinguish the series for which homogeneous nucleation (respectively heterogeneous) occurs and consequently to compute the parameter $A$ relative to each type of phenomenon. For all the series, whatever the nucleation, the growth rate is identical, which implies that the parameters of growth, that are $k_y$ and $g$ take relevant values. The optimization results of the parameters $A$, $B$, $k_y$ and $g$ (homogeneous and heterogeneous nucleation) are presented in Table 2 for the whole set of experimental runs.

The range of $g$ is found between 1.46 and 1.68 [29] but does not consider the type of nucleation. The value of $g$ equal to 1.34 in our experiments exhibits the same order of magnitude but is slightly lower. Experimental and calculated supersaturation values are compared in Figs. 6a–6c and 7a–7d for various initial supersaturation values corresponding both to homogeneous and heterogeneous nucleation. The feasibility of the method proposed here is demonstrated since it is possible to obtain parameters in agreement with the actual evolution of supersaturation in the reactor, thus leading to parameters of nucleation and growth that are consistent with thermodynamics. It can be observed that a very close agreement between the experimental supersaturation and the predicted one is obtained. From a numerical point of view, the methodology is more stable when calculating the parameters of the nucleation rate and growth for all series simultaneously.

![Fig. 3. Evolution of induction time logarithm vs. supersaturation.](image)

**4.5. Reconstruction of size distribution**

The results obtained by the numerical method of reconstruction of the size distribution are now compared with those obtained with experimental analysis, i.e., laser granulometry and morphometry. It must be emphasized that laser granulometry is not well-suited for considering non-spherical crystals. It is yet necessary to take into account the shape of crystals and the mode of growth. For this purpose, some images of the obtained crystals are achieved by means of Scanning Electron Microscope SEM. The observations (Fig. 8) confirm that crystals of big size are obtained (up to 180 µm) and also show the formation in large quantities of crystal aggregates of small size. The aggregation phenomenon is probably the origin of the difference in the forms of the size distribution. During aggregation, crystal growth is not due to the surface growth of the crystal but to an addition of crystals of small size.

Morphometry, based on image analysis principle, as well as SEM characterizes particles by providing high-quality images that are very precise from a statistical point of view on the size and particle shape. Morphometry G3 is an ideal technology to detect the presence of an extremely low number of particles or foreign bodies. The particle size, which can be measured ranges between 0.5 µm and 3000 µm. For each experimental series, it is possible to reconstitute the final size distribution numerically, by using the abovementioned procedure for the experiments with either homogeneous or heterogeneous nucleation (Fig. 9). The results are then compared with those obtained by laser granulometry for homogeneous and heterogeneous nucleation (Fig. 10). The modeled size distribution is also compared with the morphometric analysis (Fig. 11). It can be pointed out that the particle sizes provided by laser granulometry are larger than those predicted by the numerical approach. Moreover, the size distribution exhibits different shapes for experiments and simulation runs. The maximum volumetric percentage corresponds to the maximum size predicted by the model of reconstruction of size distribution. The volumetric percentage predicted by the model of reconstruction and that obtained by laser granulometry are identical. The size distribution form obtained by morphometric analysis (Fig. 11) is closer to that

![Fig. 4. $B$ and $k_y$ parameters sensitivity with $A$ value for homogeneous nucleation.](image)

![Fig. 5. $B$ and $k_y$ parameter sensibility with $A$ value for heterogeneous nucleation.](image)

**Table 1**

<table>
<thead>
<tr>
<th>Parameter</th>
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<th>Heterogeneous</th>
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<tr>
<td>$A$ ($m^{-1} s^{-1}$)</td>
<td>$10^9$</td>
<td>$10^{10}$</td>
</tr>
<tr>
<td>$B$</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>$k_y$ (m/s)</td>
<td>$10^{-7}$</td>
<td>$10^{-7}$</td>
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<tr>
<td>$g$</td>
<td>1</td>
<td>2</td>
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Table 2
Kinetic parameters of homogeneous and heterogeneous nucleation and growth:

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<th>Homogeneous Nucleation and growth</th>
<th>Heterogeneous Nucleation and growth</th>
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<td>$10^{7.47}$</td>
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<tr>
<td>$B$</td>
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<td>$k_2 \text{ m/s}$</td>
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</tr>
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<td>$g$</td>
<td>1.34</td>
<td>1.34</td>
</tr>
</tbody>
</table>

Fig. 6a. Comparison of the predicted and experimental values with time for homogeneous primary nucleation (pH initial = 9.6, [NH$_4$] = [PO$_4$] = [Mg] = 4 mmol/l, Sr initial = 2.43).

Fig. 6b. Comparison of the predicted and experimental values with time for homogeneous primary nucleation (pH initial = 9.25, [NH$_4$] = [PO$_4$] = [Mg] = 4 mmol/l, Sr initial = 2.09).

Fig. 6c. Comparison of the predicted and experimental values with time for homogeneous primary nucleation.

Fig. 7a. Comparison of the predicted and experimental supersaturation for heterogeneous primary nucleation (pH initial = 9.16, [NH$_4$] = [PO$_4$] = [Mg] = 3 mmol/l, Sr initial = 1.44).

Fig. 7b. Comparison of the predicted and experimental supersaturation for heterogeneous primary nucleation (pH initial = 8.6, [NH$_4$] = [PO$_4$] = [Mg] = 4 mmol/l, Sr initial = 1.26).

Fig. 7c. Comparison of the predicted and experimental supersaturation for heterogeneous primary nucleation (pH initial = 8.5, [NH$_4$] = [PO$_4$] = [Mg] = 3 mmol/l, Sr initial = 0.87).

Fig. 7d. Comparison of the predicted and experimental supersaturation for heterogeneous primary nucleation.
obtained by the reconstruction model. The volumetric percentage from morphometric analysis is lower than that given by laser granulometry or predicted by the reconstruction model.

An important parameter concerns the size of the crystals that are mainly produced during crystallization. Table 3 presents the comparison between the crystal size produced during the experiments (the size corresponds to the maximum value of the volumetric percentage) and the values obtained by the numerical method of reconstruction of size distribution. It can be highlighted that the method of reconstruction in the case of a heterogeneous nucleation induces a better precision level. The difference between model results and experiments is more important in the case of homogeneous nucleation.

More generally, the results obtained by morphometry are closer to the results of the reconstruction model. In case of heterogeneous nucleation, the accuracy lies between 1% and 5%, and in case of homogeneous nucleation, the accuracy is between 15% and 20%.

The variation is much more important when comparing with the results given by laser granulometry: for heterogeneous
Table 3
Comparison between the crystal size corresponding to the maximum value of volumetric percentage (mode of the distribution obtained for the experiments with the reconstruction model).

<table>
<thead>
<tr>
<th>Morphometry (µm)</th>
<th>Laser granulometry (µm)</th>
<th>Model size (µm)</th>
<th>Deviation between model and morphometry measurement (%)</th>
<th>Deviation between model and laser granulometry measurement (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Homogeneous nucleation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr = 2.43</td>
<td>58</td>
<td>89</td>
<td>49</td>
<td>15.71</td>
</tr>
<tr>
<td>Sr = 2.09</td>
<td>66</td>
<td>80</td>
<td>53</td>
<td>19.70</td>
</tr>
<tr>
<td>Sr = 1.86</td>
<td>68</td>
<td>71</td>
<td>55</td>
<td>19.12</td>
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<tr>
<td>Heterogeneous nucleation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr = 1.44</td>
<td>74</td>
<td>90</td>
<td>70</td>
<td>5.41</td>
</tr>
<tr>
<td>Sr = 1.06</td>
<td>68</td>
<td>71</td>
<td>67</td>
<td>1.47</td>
</tr>
<tr>
<td>Sr = 0.87</td>
<td>62</td>
<td>70</td>
<td>64</td>
<td>-3.23</td>
</tr>
</tbody>
</table>

nucleation, the accuracy is between 5% and 22%, and in case of homogeneous nucleation, the accuracy is between 20% and 45%.
These results demonstrate the possibility to predict the distribution and the maximum size of crystals with a numerical reconstruction of particle size distribution, starting from nucleation and growth kinetics determined in a stirred reactor.

4.6. Determination of optimal supersaturation for struvite growth

The design of an efficient process for water treatment requires the production of crystals of important size to avoid a subsequent filtration stage, with relatively low concentrations of phosphates, ammonium and magnesium and, consequently, a minimal supersaturation of the solution. The reconstruction model of the size distribution predicts the maximum size that struvite can reach according to the initial conditions. The type of nucleation influences the final crystal size (see Fig. 12). For homogeneous nucleation, an increase in relative supersaturation results in a decrease in the maximum crystal size obtained while the volumetric percentage yet increases. Conversely, for heterogeneous nucleation, an increase in relative supersaturation involves an increase in the maximum crystal size while the volumetric percentage yet decreases. It can be deduced that there exists a compromise between the maximum crystal size and a minimal supersaturation value, corresponding to a value of intermediate supersaturation between homogeneous and heterogeneous nucleation. The reconstruction model of the size distribution makes it possible to carry out a study of the maximum crystal size sensibility obtained in function of relative supersaturation.

Fig. 12 presents the maximum crystal size predicted by the reconstruction model of size distribution vs. relative supersaturation. It can be observed that a relative supersaturation of 1.455 leads to a maximum crystal size of 69.5 µm, which also corresponds to the maximum volumetric percentage of the produced crystals.

5. Conclusion

The crystal size distribution prediction is a cornerstone to control the quality of a precipitated product. For this purpose, a population balance to predict the particle size distribution was developed and a simplified nucleation-growth crystal formation was studied, based on a one-dimensional model of batch crystallization.

A new strategy has been implemented for a robust determination of the parameters of nucleation and growth, coupling a thermodynamic model which was developed in previous investigations with a population balance equation. An optimization procedure based on the minimization of squared difference between supersaturation predicted by the model of growth and the value obtained from experiments was implemented in order to identify the parameters of nucleation and growth.

The results are in agreement with the evolution of supersaturation along time in the reactor. From a numerical point of view, this approach has proved to be more stable numerically when considering all the experimental series for identifying the parameters of nucleation rate and growth. These parameters were then used to predict the size distribution using a method of reconstruction. The shape of the crystal size distribution obtained by calculation is typical of a nucleation-growth model where the growth phenomena of aggregation and breakage of the crystals are neglected. The reconstruction method also exhibits a good agreement with the curves of size distribution obtained by laser granulometry and morphometry. The results obtained by morphometry are more realistic and closer to the results of the reconstruction model: for heterogeneous nucleation, the accuracy is between 1% and 5%, and in the case of homogeneous nucleation, the accuracy is between 15% and 20%.

These results are of major importance for the design of struvite precipitation reactor and for the development of crystal growth control methodology.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ccej.2012.10.038.

References


