Assessing the effects of intra-granule precipitation in a full-scale industrial anaerobic digester


ABSTRACT

In this paper, a multi-scale model is used to assess the multiple mineral precipitation potential in a full-scale anaerobic granular sludge system. Reactor behaviour is analysed under different operational conditions (addition/no addition of reject water from dewatering of lime-stabilized biomass) and periods of time (short/long term). Model predictions suggest that a higher contribution of reject water promotes the risk of intra-granule CaCO₃ formation as a result of the increased quantity of calcium arriving with that stream combined with strong pH gradients within the biofilm.

The distribution of these precipitates depends on: (i) reactor height; and (ii) granule size. The study also exposes the potential undesirable effects of the long-term addition of reject water (a decrease in energy recovery of 20% over a 100-day period), caused by loss in biomass activity (due to microbial displacement), and the reduced buffer capacity. This demonstrates how both short-term and long-term operational conditions may affect the formation of precipitates within anaerobic granules, and how it may influence methane production and consequently energy recovery.

Key words | ADM1, biofilm, industrial wastewater, multiple mineral precipitation, physico-chemical modelling, space competition within granules

NOMENCLATURE

\( a_i \) Chemical activity
\( A_k \) Area of the sphere at point \( k \)
ADM1 Anaerobic Digestion Model No. 1
BSM2 Benchmark Simulation Model No. 2
\( C \) Carbon
Ca Calcium
CaO Lime
CaCO₃ Calcite
CH₄ Methane production (gas) (m³.d⁻¹)
CO₂ Carbon dioxide production (gas) (m³.d⁻¹)
COD Chemical oxygen demand
\#.D Data set for model testing
EtOH Ethanol
H Hydrogen
H₂S Sulfide production (gas) (m³.d⁻¹)
\( H_3PO_4^{5-} \) Phosphate measurements (g P.m⁻³)

\( I \) Ionic strength
IC Internal circulation
ISS Inorganic suspended solids (g.m⁻³)
K Equilibrium constant
\( k_{cryst} \) Crystallization rate
\( K_{sp} \) Solubility product constant
L Biofilm thickness (m)
\( L_{max} \) Maximum biofilm thickness (m)
M Mixing section
Mg Magnesium
\( n_{part} \) Number of particulates
N Nitrogen
NaOH Sodium hydroxide
NH₃ Ammonium/ammonia measurements (g N.m⁻³)
O Oxygen
P Phosphorus

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**Introduction**

Anaerobic technologies are popular treatment options within the wastewater engineering field since they: (1) ensure compliance with the effluent discharge limits; (2) produce biogas that can be converted to energy (heat/electricity/vehicle fuel) to reduce the power demands within the treatment facility; and (3) avoid nutrient destruction enabling its potential capture in different forms and qualities. Addressing these goals has led to widespread use of the International Water Association (IWA) Anaerobic Digestion Model No. 1 (ADM1) (Batstone et al. 2002) for design, control, benchmark and optimization of anaerobic technologies, as well as investigation of controlling mechanisms (Donoso-Bravo et al. 2011). Indeed, anaerobic digestion models have moved beyond the original scope of the ADM1, and are being expanded to describe a broader range of technologies (lagoons/waste stabilization ponds, high-rate system plug flow reactors ...), new processes and also in response to the general need to consider anaerobic systems in a much broader context (Batstone et al. 2015; Puyol et al. 2017).

There is a growing interest within the wastewater treatment plant modelling community to correctly describe physico-chemical processes after many years of mainly focusing on biokinetics (Barat et al. 2013; Flores-Alsina et al. 2015; Lizarralde et al. 2015; Solon et al. 2015; Huber et al. 2017; Vaneckhaute et al. 2017). Future modelling needs, such as development of resource recovery strategies via simulations (Puyol et al. 2018), will require better descriptions of cationic/anionic behaviour, multiple mineral precipitation and gas–liquid mass transfers (Batstone et al. 2012; Kazadi Mbamba et al. 2015a, 2015b; Lizarralde et al. 2018). Another important niche where improved physico-chemical frameworks are becoming useful is within model-based analysis of industrial water treatment systems. This is mainly due to the hostile characteristics of industrial wastewater, i.e. unbalanced COD/N/P/S ratios and high contents of salts (Dereli et al. 2010; Barrera et al. 2014; Feldman et al. 2017). These characteristics are very distant from domestic wastewater conditions upon which some of the standard models (Henze et al. 2000; Batstone et al. 2002) were developed, often heavily dominated by input ions.

In biotechnology industries producing wastewater streams with high content of salts, the formation of multiple mineral precipitates can cause the accumulation of inorganic particulates at different locations in the reactor (granules, pipes), which might lead to detrimental (loss of methanogenic activity) or even catastrophic (cementation) effects on reactor performance (Van Langerak et al. 1998, 2000). The formation of precipitates in either bulk or biofilm, for example in anaerobic granular sludge systems, may depend on many factors, such as cationic/anionic load, degree of influent acidification and/or granule size. The potential assessment (a priori) of the conditions promoting the formation of multiple mineral precipitates is of paramount importance for process engineers.
deciding amongst competing operational procedures when optimizing plant performance.

A multi-scale model-based approach was previously developed describing the reactor performance in terms of influent and effluent conditions such as chemical oxygen demand (COD), volatile fatty acids (VFA), nutrients and minerals, and biogas production as well as the microbial content of the granules. The model was able to reproduce the effluent concentrations and biogas production from two separate data sets (Feldman et al. 2017). The current paper extends this work to evaluate the impact of elevated calcium levels, and further explores the impact of precipitation on granule structure and activity at longer time frames, specifically through displacement of active microbial biomass via precipitates when ionic inputs increase through use of saline reject water.

The main objective of this study is to use the previously mentioned model-based approach: (1) to assess the potential formation of intra-granule mineral precipitation in industrial anaerobic reactors; (2) to describe the spatial competition between biomass inorganic particulates within granules; and (3) to evaluate the effect of mineral precipitation on COD conversion and potential energy recovery. The paper details the application of a previously published multi-scale model to simulate the effects of calcium-rich reject water specifically accounting for how growth/decay of microorganisms and formation of inorganic precipitates compete for space.

**METHODS**

**Plant configuration and data measuring campaign**

The plant under study is located in Kalundborg in the north-western part of Zealand (Denmark) and treats the wastewater produced at Novozymes and Novo Nordisk. Reactor design is based on the BIOPAQ® IC technology (Paques, The Netherlands) (see Figure 1). Data from two experimental campaigns were used to test the predictive capabilities of the model. For the first data set (#D1) (no reject water) the influent characteristics are: 144 m$^3$.h$^{-1}$, 1,600 kg COD.h$^{-1}$, 70 kg N.h$^{-1}$, 40 kg P.h$^{-1}$, 47 kg Ca.h$^{-1}$, pH = 6.9 (no reject water). Data for the second period (#D2) (reject water is added) represent higher flow, COD and calcium load as a result of adding reject water: 207 m$^3$.h$^{-1}$, 2,200 kg COD.h$^{-1}$, 160 kg N.h$^{-1}$, 55 kg P.h$^{-1}$, 124 kg Ca.h$^{-1}$, pH = 7.2 (see Feldman et al. (2017) for further details). In both cases the S:COD ratio is similar (0.025 kg.kg$^{-1}$). The BSM2 influent generator (Gernaey et al. 2011)

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**Figure 1** Multi-scale model approach and proposed mechanisms to describe organics/inorganics competition for space within the biofilm.
was applied to give additional data (Martin & Vanrolleghem 2014) when few measurements were available.

**Full-scale industrial anaerobic digester reactor model**

A multi-scale, fully coupled approach is adopted as a baseline model to describe the system under study (see Feldman et al. 2017). At the reactor scale, the mixing section (M), the expanded sludge blanket (R1) and the polishing section (R2) are described as a series of continuous stirred tank reactors. At the granular scale, granule size and distribution are assumed to be dependent on reactor height as a function of TSS measurements. Larger granules \((L_{\text{max}} = 4 \text{ mm})\) are located at the bottom (M) of the reactor. The granule radius decreases \((L_{\text{max2}} = 2 \text{ mm}, L_{\text{max3}} = 0.5 \text{ mm})\) as a function of reactor height (R1, R2). This has been modified from the original implementation to have: (1) a better representation of the granular size and (2) good coverage of the different gradients within the reactor. This distribution is based on the assumption that the heaviest granules are in the bottom and lightest granule in the top. Finally, at the biofilm level, a one-dimensional model is constructed where the mass balances are derived from spherical geometry. Reaction rates in both the bulk and the biofilm are evaluated using the stoichiometry and kinetics as described in the ADM1 (Batstone et al. 2002). The default ADM1 implementation is upgraded to include phosphorus, sulfate and ethanol related conversion processes (Flores-Alsina et al. 2016).

**Biofilm growth and organics/inorganics competition for space**

The mass balance assumes that the transport of soluble compounds \((S_i)\) is governed solely by (homogenous) diffusion whereas movement of particulate compounds \((X_i)\) takes place by convection (Saravanan & Sreekrishnan 2006). Temporal change of biofilm thickness \((dL/dt)\) (Equation (1)) is given as the radial distance \((z)\) from the centre to the surface of the granule and is impacted dynamically by: (i) the net growth of the particulate species (organics, biomass + precipitates) (Equation (2)) \((u_P)\); and (ii) detachment from the biofilm surface \((u_D)\) (Equation (3))

\[
\frac{dL}{dt} = u_P + u_D
\]

\[
u_P = \frac{1}{A_k} \sum_{k=1}^{\text{max}} \sum_{i=1}^{\text{org}} \frac{r_{\text{org}} + r_{\text{biomass}} + r_{\text{precipitation}}}{\rho_{\text{biomass}}} \cdot A_k \cdot \frac{\Delta L}{\rho_{\text{biomass}}}
\]

\[
u_D = u_F \left( \frac{L}{L_{\text{max}}} \right)^2
\]

This results in a moving boundary layer and biofilm internal grid \((k)\). In Equation (2), \(A_k\) is the area of the sphere at point \(k\) and \(\rho_{\text{biomass}}\) is the density of the biomass, which is assumed to be constant for simplicity reasons. The organic/inorganic distribution within TSS is described following the principles reported in Ekama & Wentzel (2004) and Ekama et al. (2006). The detachment velocity is modelled according to Equation (3) (Lackner et al. 2008), where \(L_{\text{max}}\) is the defined maximum radius of the granule. The resulting system of partial differential equations is solved using the method of lines (Press et al. 2007). In this case, discretization of space \((z = \text{radial distance})\) is chosen to obtain a system of ordinary differential equations. The second-order space derivative describing diffusion \((S)\) only is approximated by the finite central difference method in spherical geometry (unless it is the first node, where it is a forward difference, or the last node, where it is backward difference). A similar approach is used for \(X\) convective movement. The integral in the equation describing the biofilm growth velocity is approximated by the trapezoidal rule. Further information about biofilm/bulk mass balancing, boundary conditions and numerical resolution can be found in Vangsgaard et al. (2012) and Feldman et al. (2017).

**Scenario analysis and long-term evaluation**

The proposed set of models are tested using the data sets (S1) presented in Feldman et al. (2017). Next, an additional data set is used to evaluate the effect of adding reject water (S3). Calibration procedure is also described in Feldman et al. (2017). Finally, the 3-week dynamic pattern (Gernaey et al. 2011) used to adjust the model parameters is repeated five times longitudinally (until reaching 3 months), and model predictions are analysed based on this longer time frame (S2, S4) (see Table 1).

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**RESULTS**

**Effects of adding reject water on influent/effluent characteristics and operational conditions**

Multi-scale modelling and parameter values reported in Feldman et al. (2017) in simulation scenarios S1 and S3 show that it is possible to describe the transformation of organics, nutrients and minerals; the production of methane, carbon dioxide and sulfide; and the formation of precipitates within the bulk phase for both data sets satisfactorily (see Tables 1 and 2). Both full-scale measurements and model simulations show that the immediate effect of adding reject
water is an increase of pH in the influent (Figure 2(a) and 2(b)) and a reduction of the quantity of chemicals (NaOH) used for pH control within the reactor (even though the reactor pH was higher compared to the scenario without reject water addition) (Figure 2(c), 2(d), 2(g) and 2(h)). This effect is mainly due to the addition of reject water, which creates an increase of the buffer capacity due to the presence of calcium ions (related to quicklime, CaO, use in sludge stabilization prior to dewatering). The results also show that the physico-chemical framework is capable of predicting influent/effluent pH from the influent/effluent cationic/anionic composition. Finally, the addition of COD coming from the reject water increases biogas production and consequently energy recovery by an average of 9.5% (see CH4 values in Table 2 and Figure 2(e) and 2(f)).

**Location of precipitates depends on granule size/reactor height**

Simulation results indicate a stratified structure within the granule, which is the result of: (1) applied loading rates; (2) mass transfer limitations; and (3) specific (bacterial) affinity for substrate. These phenomena have been widely/intensively studied by other authors (Picioreanu et al. 2000; Batstone et al. 2004b; Morgenroth et al. 2004; Xavier et al. 2005) As an example, using S2 and S4, the top part of Figure 3 shows the changes in the granule composition as a function of reactor height for data set #D2 (reject water is added) when reaching steady state (M, R1 and R2); i.e. we assumed 1,000 days of simulation. No inter-granule precipitation applied to reach this steady state. These initial conditions are then used to run dynamic simulations, simulating formation of intra-granule precipitates. At \( t = 0 \) d in M, the centre of the granule is inactive due to the high concentration of inert material (\( X_I \)) resulting from biomass decay. The biomass (\( X_{bio} \)) and organics (\( X_{org} \)) concentrations increase with an increasing radial distance (\( z \)), i.e. the closer to the surface of the granule, the higher the biomass concentration. The fraction of inerts (\( X_I \)) decreases at the top of the reactor, where the granule composition essentially consists of active biomass (see Figure 3). Additional simulation results show higher pH values in the centre of the granule and a significant decrease towards the surface (see Figure 3). This is mainly due to VFA, which are converted into the weaker carbonic acid leading to elevated pH.

**Table 1** | Definition of the different simulated scenarios

<table>
<thead>
<tr>
<th>Scenario</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Characteristics</td>
<td>Calcium rich (reject water)</td>
<td>Calcium rich (reject water)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Influent period</td>
<td>Short term (data-set based)</td>
<td>Long term (extrapolated)</td>
<td>Short term (data-set based)</td>
<td>Long term (extrapolated)</td>
</tr>
</tbody>
</table>

**Table 2** | Effects of adding reject water on effluent characteristics (measurements and multi-scale ADM1 model simulations)

| | \#D1 (no reject water) & \#D2 (reject water is added) |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | Measurements    | Deviation (%)   | \( R^2 \)       | Measurements    | Deviation (%)   | \( R^2 \)       |
| CH4 (gas) (Nm\(^3\).d\(^{-1}\)) | 11,015           | 4.5             | >0.7            | 12,059          | 14.3            | 0.5–0.7         |
| CO2 (gas) (Nm\(^3\).d\(^{-1}\)) | 2,922            | 1.7             | >0.7            | 3157            | 4.8             | 0.5–0.7         |
| H2S (gas) (Nm\(^3\).d\(^{-1}\)) | 178              | 25.5            | >0.7            | 206             | 12.7            | 0.5–0.7         |
| NHX (g N.m\(^{-3}\)) | 299              | 1.2             | 0.5–0.7         | 426             | 3.3             | <0.5           |
| H\(_3\)PO\(_4\) (g P.m\(^{-3}\)) | 44               | 25.17           | >0.7            | 14              | 3.2             | >0.7           |
| SO\(_4\) (g S.m\(^{-3}\)) | 97               | 14.6            | <0.5            | 111             | 10.6            | <0.5           |
| VFA (kg COD.m\(^{-3}\)) | 0.79             | 19.3            | 0.5–0.7         | 0.41            | 21.7            | <0.5           |
| COD\(_{tot}\) (kg COD.m\(^{-3}\)) | 1.73             | 18.2            | >0.7            | 1.07            | 0.22            | <0.5           |
| COD\(_{part}\) (kg COD.m\(^{-3}\)) | 1.15             | 6.2             | <0.5            | 3.06            | 6.18            | <0.5           |
| Ca (g.m\(^{-3}\)) | 332              | 3.6             | 0.5–0.7         | 520             | 24.42           | <0.5           |
| Mg (g.m\(^{-3}\)) | 29               | 1.76            | <0.5            | 26              | 9.5             | <0.5           |
| Average       | 10.2             |                  |                 |                 |                  | 10.1            |

Simulation scenarios are S1 and S3. Deviation (%) and \( R^2 \) are calculated between simulation values and plant measurements.
pH conditions. Higher influent Ca concentration and increasing intra-granular pH gradients also favour saturation conditions (higher SI) for CaCO₃ when reject water is added (see Figure 3). SI is calculated as the logarithm of the product of the reactant activities divided by the solubility product of compounds investigated (Kazadi-Mbamba et al. 2015a, 2015b).
When SI > 1 the compound is supersaturated. On the other hand, when SI < 1, the solution is assumed to be undersaturated. Similar experimental observations as described in Figure 3 were reported by de Beer et al. (1995), Flora et al. (1998), Batstone et al. (2004a) and Saravanan & Sreekrishnan (2006).

Assuming both biological activity and formation of inorganic solids, simulation results indicate a vertical gradient: high concentration of precipitates in M and R1 and lower in R2 (see Figure 4), i.e. precipitates tend to accumulate in the bottom part of the reactor. The latter corresponds with experimental observations where the content of ash in TSS (ISS/VSS ratio) decreases when moving from the bottom to the top of a bioreactor, and thus the content of biological matter increases (15% of the dry weight is in the form of VSS in the bottom of the reactor, as opposed to 69% at the top of the sludge bed). The location of precipitates depends on the granule size. In larger granules ($L_{\text{max}} > 2 \text{ mm}$), the conversion of organic acids to inorganic carbon takes place in the first 100 μm of the biofilm due to diffusion limitations. As a consequence, CaCO$_3$ precipitation tends to occur close to the surface of the granule. In smaller granules ($L_{\text{max}} < 1 \text{ mm}$) substrates diffuse to the centre of the granule; therefore, deposition of precipitates will take place in the core. This corresponds with the experimental observations described by Alphenaar et al. (1995). Due to the precipitation in the granule, $X_{\text{inorganic}}$ increases, and subsequently decreases the fraction of $X_{\text{bio}}$ in all granule sizes (Figure 3). Other factors such as loading conditions ($M, R1$ and $R2$) and pH strongly affect/contribute to the distribution of precipitation within the granule.

**Undesirable effects of long-term use of reject water**

Figure 5 shows the potential long-term effects of adding reject water (scenarios S2 and S4). Even though in the short term the effects of adding reject water are beneficial (lower use of chemicals, higher buffer capacity), in the long run, the accumulation of precipitates in the granules decreases methanogenic activity and consequently energy recovery. This is mainly due to the space occupation within the granule by inorganic (see Figure 4) precipitates that compete for space with acidogenic/acetogenic/methanogenic bacteria. As a consequence, the VFA concentration increases (197%) and CH$_4$ production decreases by 20% from the first 18 days to the last 18 days in a 100-day simulation period (see Figure 5). This corresponds to the experimental observations reported by Keenan et al. (1995), El-Mamouni et al. (1995) and Van Langerak et al. (1998) when comparing anaerobic systems with different levels of precipitation.
DISCUSSION

Main achievements and limitations

Inactivation of mineral precipitates in industrial high-rate anaerobic reactors is one of the main challenges in application of this technology to high-calcium or magnesium wastewaters. These are widely distributed, and include paper mills (van Langerak et al. 1998; Batstone & Keller 2003) and beet sugar factories as well as the potato and wheat starch industry (Austermann-Haun et al. 1999). The issues are well known, and mitigation strategies include the use of calcium carbonate pre-precipitation (van Langerak et al. 1998), or the periodic reseeding of reactors. Model-based analysis has been previously used to optimize these systems (Batstone et al. 2002), but the ability to predict the trajectory of granule inactivation substantially enhances the ability to optimize mitigation processes. Predicting both the growth/decay of microorganisms simultaneously with the potential formation of inorganic precipitates within the granule, resulting in space competition in the biofilm, does involve a complex implementation with a number of underlying biochemical (Batstone et al. 2002; Flores-Alsina et al. 2016), physico-chemical (Kazadi Mbamba et al. 2015a, 2015b) and speciation models (Flores-Alsina et al. 2015) in the bulk phase and each discretized layer of the biofilm (Wanner et al. 2006), but allows the description of these critical phenomena.

Decision support tool within the treatment facility

The company involved in the study has experienced an increased use of salts in the production process, and these salts could potentially disturb the proper operation of the anaerobic digestion processes at the wastewater treatment plant. There is therefore an interest in investigating the effects of high salt concentrations (e.g. sulfate, calcium, phosphate) on the performance of anaerobic digestion processes in more detail. The mathematical model developed in this study can be used as a decision support tool (Liu et al. 2008) for implementing strategies to control precipitation kinetics within granules, i.e. modification of the operational pH without losing methanogenic activity.

Another potential option explored is model-based evaluation of the addition of other salts instead of NaOH (for example MgO and CaO (Jeison et al. 2008). Such scenario analysis can be helpful for predicting the impact of increased use of a specific salt in the production process. The addition of chemicals for pH control has a significant impact on the overall reactor performance. Feldman et al. (2018) showed that a saving in operating costs of about €0.88 million/year/year can be obtained by decreasing the pH in the reactor by up to half a pH unit compared to the default operational values that were used at full-scale (ensuring the same methane yield). Thus, on top of energy recovery, the potential formation of precipitates can be included in order to have a more informed assessment. An excessive formation of precipitates may force the company to purchase new (granular) biomass, which is a considerable financial expenditure.

Model validation through activity testing and molecular analysis

The impact of precipitation on granule activity and structure has been previously documented (van Langerak et al. 2000;
Saunders et al. 2002; Jeison et al. 2008). The results reflect those found in the current paper. However, the trajectory of precipitation formation and variation with location allows further opportunity for validation. Preliminary work on the target system using biomass activity tests and 16S rRNA amplicon sequencing has supported simulation results with a higher concentration of mineral precipitates and reduced activity from samples taken at the bottom of the reactor (Prevedello et al. 2018). A decrease of the methanogenic activity, together with a reduced abundance of methanogenic Archaea and lower biomass concentration were observed.

CONCLUSION

- The study shows the potential effects of continuous intra-granule precipitation within the reactor and how acidogenic/acetogenic/methanogenic activities can be affected. The study demonstrates how an initially good operational option can become less desirable when evaluated over a long period.
- High alkalinity of the reject water stream increases influent pH and reduces the quantity of NaOH used for pH control within the reactor. In addition, the extra COD load initially increases biogas production and consequently energy recovery by 9.5%.
- Simulation results reveal a 20% loss in activity over a longer time period as result of the formation of precipitates. The latter accumulate at the bottom of the reactor and change depending on the granule size. Thus, in larger granules, CaCO₃ is expected to form in the outer layers of the granule. In smaller granules precipitates will tend to spread all the way to the centre of the granules.

SOFTWARE AVAILABILITY

The Matlab-Simulink code of the model presented in this paper is available upon request, including the implementation of the physico-chemical (PCM) and biological (ADM1) modelling framework in granular sludge reactors (BIOFILM). Using this code, interested readers will be able to reproduce the results summarized in this study. To express interest, please contact Professor Krist V. Gernaey (kvg@kt.dtu.dk) or Dr Xavier Flores-Alsina (xfa@kt.dtu.dk) at the Technical University of Denmark.

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