WEFTEC® 2012 Technical Session Proposal Form

IMPORTANT NOTE: Please complete all items. This outline is formatted to complete on a computer and does not leave adequate room for hand-written responses.

Submitted by: Eugenio Giraldo, Eugenio.giraldo@amwater.com

Organizing WEF Committee (or Other Group): Municipal Wastewater Treatment Plants Design (knowledge development subcommittee and MEGA) and Residuals and Biosolids- Bioenergy

Supporting WEFTEC Program Committee Symposium: Research Symposium and Biosolids Symposium

SESSION DESCRIPTION

Proposed Session Title: Anaerobic Digestion Modeling. Review of Knowledge Gaps and Proposals for Moving Forward

Session Format: (check one): Platform ____________
Panel Discussion ________
Combination of Both X

Brief session description (to be used to judge the session and in publicity if selected; a paragraph or two is adequate, but more can be provided if needed):

Is this session on a “hot” topic? YES X NO
Why? Anaerobic Digestion is the most widely used process for energy recovery from wastewater, with current emphasis on green house gas reduction, sustainability and energy neutrality AD plays a central role. However, some key aspects of the digestion process are not adequately incorporated in existing models, e.g. thermophilic digestion, codigestion, stability, anaerobic sewage treatment, physicochemical processes. The present group of papers will review existing practice on these key topics, identify knowledge gaps and innovative proposals for modeling and route the way forward. A panel discussion will also be included to obtain feedback from practitioners regarding modeling needs of anaerobic digestion processes. The topic also has high relevance for Latin-America.

How is the information in this session different or unique from what may come from the call for abstracts? It is a coordinated review tackling key aspects of the process that would not come together as part of the regular call for abstracts.

Session keywords: (List or select from attached list) Anaerobic Digestion, Modeling, Bioenergy, Green house gases, Energy Neutrality, sustainability
AUDIENCE INFORMATION
Who is the target audience for this session? (List or select from attached list)
1. Municipal/District Water and Wastewater Systems and/or Plants
2. Municipal/District Wastewater Only Systems and/or Plants
4. Industrial Systems/Plants (Manufacturing, Processing, Extraction)
5. Consulting or Contracting Firm (e.g., Engineering, Contracting and Environmental)
6. Government Agency (e.g., US EPA, State Agency, etc.)
7. Research or Analytical Laboratories
8. Educational Institution (Colleges and Universities, Libraries and other related organizations)
9. Manufacturer or Water/Wastewater Equipment or Products

Does this session apply to professionals in water, wastewater, or stormwater?
(circle all that apply)
WATER       WASTEWATER       STORMWATER

Estimated Attendance:  60 persons

SESSION DETAILS
Will this session require different set up (standard is theater seating, podium, head table seating for 2 people, 1 LCD projector/screen)? YES   NO   If yes, why and what is needed?

Is this a full session or half session? FULL   HALF
A full session consists of 3 hours of presentations with a ½ hour break in the middle; half sessions are 1 ½ hours with no break.

Will all speakers provide a manuscript for the proceedings? YES   NO   If no, please justify.

Will any speaker require any assistance (registration for the session, etc.)? YES   NO
If yes, please justify.

Proposed Moderator: Please note that we will send all future correspondence regarding this session to the moderator unless you specifically request here that someone else be included on all communication.

Name: Eugenio Giraldo   Email: eugenio.giraldo@amwater.com

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Name: Sudhir Murthy   Email: Sudhir.Murthy@dcwater.com

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Name: Jose Jimenez   Email: Jianmenez@brwnca.com

Proposed Speakers and Topics:
Please list each speaker, and include a one to three page abstract in this proposal for each topic or speaker in the session. If this is a panel, please include the list of speakers and any more detail needed for their topics.
Speaker 1:
Name – Jose Jimenez
Affiliation – Brown and Caldwell
Title of Presentation – Anaerobic Wastewater Treatment Modeling: a Collaborative Review and Framework for Future Work.
Email: JJimenez@brwncald.com

Speaker 2:
Name – Imre Tacaks
Affiliation – Dynamita
Title of Presentation – Modeling Physico-Chemical Processes in Anaerobic Digestion
Email: imrefiu@gmail.com

Speaker 3:
Name – Chris Wilson
Affiliation – Greeley and Hansen
Title of Presentation – Linking biosolids stability indicators to anaerobic process models for practitioners: What is known, knowledge gaps, and required research
Email cwilson@greeley-hansen.com

Speaker 4:
Name – Bernhart Wett
Affiliation ARAconsult, Unterbergerstr.1, A-6020 Innsbruck,
Title of Presentation – Anaerobic model for high-loaded or high-temperature digestion
Email bernhard.wett@uibk.ac.at

Speaker 5:
Name – Eugenio Giraldo
Affiliation – American Water
Title of Presentation – Modeling Anaerobic Codigestion of Organic Materials. State of the Art Review of current practices and modification needs for practical applications
Email: Eugenio.giraldo@amwater.com

ACKNOWLEDGEMENTS
By submitting this, I agree that I have informed the proposed speakers that all are required to prepare a paper for the proceedings, meet all deadlines associated with the presentation, and are responsible for associated registration, transportation, and housing fees, unless an exception is specifically requested above and granted by WEF before final acceptance of this proposal. Moderators and Assistant Moderators have also been informed that they are responsible for their own registration, transportation, and housing fees.

Submitter sign here:
Eugenio Giraldo
Introduction

It is undeniable that interest for anaerobic wastewater treatment is rapidly growing (McCarty et al. 2011). During the last years, there has been a renewed interest in energy use optimization, green house gas emissions reduction and recovery of resources (clean water, nutrients and energy) from wastewater treatment plants. Anaerobic processes play a prominent role for achieving all these goals. High-rate anaerobic processes such as the upflow anaerobic sludge blanket (UASB) reactors are used as an advanced primary treatment to reduce organic loading to activated sludge processes downstream and to recover methane from primary treatment.

However, process design and operation are still empirical in nature. Greenhouse gas emissions from dissolved methane (McCarty et al. 2011) and odors and toxicity effects to downstream processes from reduced sulfur compounds (Sears et al. 2004) in UASB reactors are questionable and need to be appropriately quantified and managed in plant design.

Objective

The WEF Task Group in Process Tools for Design and Operation of Anaerobic Processes has focused on conducting a literature review to address the use of anaerobic models applied to domestic wastewater systems, and evaluates future requirements for models that need to address the key motivations of operational analysis, technology development, and model-based design for these systems.
Mathematical modeling of anaerobic systems

Mathematical modeling of wastewater treatment processes plays an outstanding role as a tool capable of providing diagnostics that will give support to the plant operation and the decision-making process. Batstone (2006) conducted a comprehensive literature review on mathematical modeling of anaerobic wastewater systems. Therefore, this work expands on such review and fills the gaps and lays down the foundations for good modeling practice for anaerobic wastewater systems.

Anaerobic wastewater treatment modeling is still an emerging field. In many instances anaerobic digester models such as ADM1 (Batstone et al. 2002) and ASDM (Barker and Dold 1997) have been used as base models and adapted to simulate in isolation anaerobic wastewater treatment systems for steady-state simple solutions without considering possible issues to downstream processes (activated sludge). Most papers assessing kinetics in anaerobic wastewater systems have so far been single-step first order models (and also mostly steady state) to determine average removal rates in anaerobic reactors (Figure 1). Retention of solids in UASB reactors has been most commonly modeled by fixing solids retention time to a constant in a stirred tank reactor (Batstone et al. 2002). This, while practical, and computationally efficient, is awful for modeling effluent solids concentration dynamics. To maintain a constant SRT, effluent solids decrease in a response to simulated increase in flow which is the opposite of reality. Therefore, such models can only be used for modeling dynamics of effluent soluble components.

Existing anaerobic models can be effective at describing retention of sludge, substrate removal rates and conversion of substrate to biogas. However, they are ineffective at describing fate of nutrients through the process (especially phosphorus), solids-liquid separation and sludge behavior, supersaturation of dissolved gases and reduced sulfur compounds which are key
parameters for the proper design and operation of these systems. Therefore, this study recommends critical integration of these different modeling components into a single base model such as ADM1.

Where should we go?

Figure 2 presents, in a simplistic way, the elements for a proposed anaerobic reactor model. The future critical issues in modeling of high-rate anaerobic systems probably include hydraulics, sludge behavior, supersaturation of dissolved gases, production of soluble inert material, and sulphate reduction.

The behavior of biomass, and substrate particles need to be separated. At least a two-stage model (hydrolysis and bioconversion) is required to model these systems. A two-stage model allows predictions of organic acids, and mixes between soluble/particulate effluent fractions, and is nominally compatible with activated sludge.

References: A complete list of reference will be included in the manuscript
Figure 1: COD removal at different sludge age from an upflow anaerobic sludge blanket reactor

Figure 2: Basic elements of an anaerobic reactor model
MODELLING PHYSICO-CHEMICAL PROCESSES IN ANAEROBIC DIGESTION

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Significance
The physico-chemical element of a unified model framework is presented that is fundamental for the performance prediction of various anaerobic digestion systems – including mesophilic, thermophilic and highly loaded thermally hydrolys ed sludge digestion. pH, ionic strength and temperature dependent dissociation reactions, alkalinity, gas transfer and precipitation all need to be considered. The importance of the effect of these on product (biosolids and biogas) quality through biokinetic reactions and gas transfer will be demonstrated.

Introduction
Anaerobic digestion is a widespread and economic process for waste treatment and energy recovery. A complete process model which describes performance of the anaerobic unit necessarily contains all three phases: liquid, gas and solid (precipitates) (Harding et al, 2011). Components in the gas phase are in a dynamic equilibrium with important ionic species in the liquid phase, such as H₂CO₃ (and significant for NH₃ on higher pH levels). In the liquid phase, the biokinetic and physicochemical reactions are interlinked. The biokinetic processes act on chemical species which are active regulators and participants in the biological reactions, as well as in chemical equilibrium, redox, gas transfer and kinetic chemical precipitation processes. Certain chemical elements are kinetically linked to the precipitating/dissolving solid phase, most importantly various metal sulphide, carbonate, hydroxide, phosphate and ammonium phosphate precipitates.

The complexity of the physico-chemical system and its model is significant. A complete modeling approach has already been outlined (Batstone et al., 2002, Takács et al., 2004, Batstone
et al., 2010). This review paper will contribute by outlining and validating the complete approach specifically for various anaerobic digestion processes.

**Physico-chemical model elements for anaerobic digestion**

A general model for anaerobic digestion needs to consider the following chemical species in the liquid phase:

- **Cations:** Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), Fe\(^{2+}\) (and Al\(^{3+}\) if dosed)
- **Anions:** Cl\(^-\), HS\(^-\)
- **Weak acids/bases:** carbonate, phosphate, ammonia system, organic acids (1-4 C)
- **Precipitates:** CaCO\(_3\), MgNH\(_4\)PO\(_4\), Ca-phosphates (e.g. amorphous calcium phosphate and hydroxy-apatite (ACP, HAP)), and metal hydroxides.
- **Ionic pairs,** particularly at higher (typical digester) concentrations

The chemical speciation requires:

- Stability (logK and logKp) constants for all reactions
- Temperature correction of the stability constants according to empirical functions or the theoretical van ’t Hoff equation and standard enthalpy change (\(\Delta H^\circ\)). This is required to be able to describe higher temperature systems as temperature has a significant effect on ionization.
- Ionic strength correction according to the Debye-Hückel law. Ionic strength (causing non-ideal behaviour) in digesters is high and may be outside the validity of the simplified correction function, and as such it requires experimental adjustment.
- Consideration of each ionic species within the pH range of interest. For example in the phosphate system H\(_2\)PO\(_4\)^- and HPO\(_4^{2-}\) may be adequate to consider in typical pH ranges, but in a fermenter H\(_3\)PO\(_4\) may become significant and in a high loaded, high pH system, particularly if struvite precipitation is considered, PO\(_4^{3-}\) is important.
- Kinetic considerations, specifically for precipitation reactions (logKp’s describe the equilibrium status but not how long it takes to get there, i.e. nucleation, flocculation, surface crystallization, etc.)
- Gas transfer kinetics for CO\(_2\) and H\(_2\)S

From the process standpoint important aspects are:

- Solids loading, N and P content of the feed and process temperature are the key driving variables (provided by measurements or an activated sludge biokinetic model) for conditions within the anaerobic digester. This is illustrated in Figures 1-4.
Inhibition of biological reactions by free ammonia. Mesophylic sludge digestion systems typically do not experience ammonia inhibition (typical TSS range is 4 to 6 % in the feed). In high loaded digestion systems (organic solid waste digestion or sludge digestion systems using pre-treatment processes) the ammonia concentration can exceed the toxic ammonia level of about 2500 mg NH₄-N/L. At this concentration level and corresponding high pH the free ammonia inhibits methanogenic growth (Angelidaki et al., 1993).

Biokinetic metabolic activity relates to unionised species such as undissociated acetic acid as substrate and unionized ammonia as inhibitor.

The effectiveness of iron dosing to suppress odours caused by H₂S depends on accurately calculating free H₂S available through the chemical equilibrium system, and on gas transfer processes.

The potential to recover P by struvite precipitation can be evaluated by the comprehensive model

References
In the following figures, open markers (□, Δ), denote system without struvite precipitation and closed markers (■, ▲, ▼) denote with struvite precipitation. Biomass P content = 0.025 and PAO PP content = 0.29.

**Figure 1:** Change in alkalinity (□, ■) H$_2$CO$_3$ alkalinity (Δ, ▲), H$_3$PO$_4$ alkalinity (▼, ▼) (all in mol/L)
Figure 2: Change in effluent ortho-P concentration (○,● in mgOP-P/L) (left) and partial pressure of CO₂ (pCO₂ ○,●) and digester pH (□,■) (right) versus OHO and PAO N content (fN) from 0.05 to 0.20.

Figure 3: Change in alkalinity (□,■), H₂CO₃ alkalinity (Δ,▲), H₃PO₄ alkalinity (▼,▼) (all in mol/l) and effluent OP concentration (○,● in mgOP-P/L) (left) and partial pressure of CO₂ (pCO₂ ○,●), as well as digester pH (□,■) (right) versus OHO and PAO P content (fP) from 0.01 to 0.05.
Figure 4: Change in alkalinity. (□,■) H$_2$CO$_3$ alkalinity (Δ,▲), H$_3$PO$_4$ alkalinity (○,▼) (all in mol/l) and effluent OP concentration (○,● in mgOP-P/l) (left), partial pressure of CO$_2$ (pCO$_2$ ○,●) and digester pH (□,■) (right) versus OHO and PAO P content (fP) from 0.01 to 0.05.
Introduction

In addition to the understanding of the energy benefits and resource recovery opportunities associated with anaerobic digestion for solids management, anaerobic processes are likely to play a larger role in mainstream wastewater treatment in the future. The Anaerobic Digestion Process Tools Task Group was established by the Water Environment Federation to review and condense the current practice in AD and to develop tools for design and operation that fit the current and future practice of anaerobic digestion in the wastewater industry.

A topic of interest within anaerobic processes is the identification of suitable stability indicators. Indicators such as volatile solids destruction are currently applied biosolids with reduced vector attraction characteristics. There is a greater understanding of anaerobic process impacts on biosolids odor generation, fugitive methane emissions, residual biodegradable organics, etc. that has been developed through recent research efforts. This understanding suggests that more refined and mechanistic stability indicators are required to adequately describe biosolids stability and provide opportunities for integration into anaerobic process tools.

This paper review of the state of the art regarding biosolids stability indicators, especially as they relate to modeling tools for Anaerobic Digestion Processes. As a result, the Task Group will develop proposed modifications to existing modeling practice to incorporate perceived critical needs for practitioners seeking to assess stability issues to process tools.

What is known

The stability of biosolids produced through anaerobic digestion processes is defined in terms of the reduction of vector attraction. While numerous factors may impact vector attraction, biosolids instability is most often associated with malodors stemming from residual biological activity. In turn, residual biological activity in digested biosolids is considered to be related to the presence of readily degradable material within the biosolids after digestion. Evidence of this link can be found in CFR 40 Part 503.33 which defines biosolids stability requirements for land application via vector attraction reduction.

The most common method for meeting vector attraction requirements for anaerobically digested biosolids per Federal regulations is to achieve 38% volatile solids reduction throughout the solids treatment processes. In certain scenarios, such as extended aeration systems, where 38% volatile solids reduction is unachievable by anaerobic digestion, the regulations make provisions for bench testing to show the lack of presence of readily degradable material within the biosolids after digestion. Biosolids are routinely assessed on the basis of solids degradation as a surrogate for stability.
WEF and WERF, as well as several treatment utilities, have supported substantial research into the causes and occurrence of biosolids odor. Assuming that biosolids odor is a proper indicator of stability and vector attraction reduction, research has shown a lack of correlation between those desired characteristics of biosolids and volatile solids reduction. The following plot (Figure 1) shows a relationship between VSR and peak total volatile organic sulfur compounds from incubations of laboratory produced biosolids through a number of anaerobic digestion processes (Wilson et al., 2009). The general lack of correlation shown here suggests that the use of volatile solids reduction as an indicator of vector attraction reduction is not fully descriptive of the residual biological processes that occur within digested and dewatered biosolids. Recent work has related the processes that result in the regrowth of pathogen indicators to those resulting in the generation of odor imparting compounds (Higgins et al., 2011), neither of which are currently considered within available anaerobic process tools. These biological process may impart instability, and need to be better understood if process models are to be applied to reliably predict stability.

An additional aspect of stability that is important when considering biosolids management is the release of fugitive methane emissions. Biosolids land application is a strongly beneficial process through, among other benefits, the sequestration of carbon within agricultural land. Residual biological activity during storage, conveyance, or after land application can convert carbon to methane and contribute to the overall carbon footprint of water quality management systems. Anaerobic process models are predictive of residual concentrations of readily degradable organic material that could reasonably lead to release of fugitive methane emissions if anaerobic conditions were provided post-digestion. For example, the following plot (Figure 2) shows a series of relationships, depending on reactor temperature, that describe the yield of volatile fatty acids during primary sludge fermentation (i.e. short SRT anaerobic digestion) as a function of solids retention time. These relationships were developed by application of the Arrhenius function to the kinetic data for methanogens and fermenters developed by O’Rourke (1968). The incorporation of existing kinetic data and understood relationships with environmental conditions could provide practitioners with means to predictively assess GHG emissions from processes downstream of anaerobic digestion.

**Knowledge Gaps and Required Research** There is clearly an existing knowledge gap concerning the mechanistic connection between standard indicators of digestion performance and standard indicators of biosolids stability. This knowledge gap is the focus of ongoing research through WERF. In addition, existing kinetic data and relationships can be better applied within process tool in order to provide services, such as predictions of stability (i.e. odors) and GHG emissions, that would provide substantial benefit to modelers and other practitioners.

This abstract provides a brief overview of the state of the art regarding biosolids stability indicators. The associated paper and presentation will provided detail on the state of the science, and provide guidance on where the state of the science on biosolids stability is being applied and where further work, either fundamental or in implementation, is needed.

The wide application and promise of anaerobic process technology presents a broad base of interest for this work with WEF and a substantial opportunity to achieve significant improvements in the applicability of process tools.
Figure 1: Relationship between solids destruction, a surrogate for biosolids stability, and biosolids odor compound generation.

Figure 2: Relationship developed from existing kinetic data and understood temperature dependency describing YFA yield during primary fermentation.
References


Anaerobic model for high-loaded or high-temperature digestion – additional pathway of acetate oxidation

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ABSTRACT

Current models cannot properly simulate processes that are operated under high loadings or high temperatures. A modification to existing models has been implemented by adding important missing degradation pathways, to accommodate these high loaded and high temperature anaerobic systems without artificially recalibrating the model parameters. This degradation pathway relies on the use of an alternate acetate oxidizing mechanism that is more tolerant to ammonia than the aceticlastic pathway. Inhibition values have been estimated and a logistic function has been used to apply ammonia inhibition. The model also relates metabolic activity to unionised species such as undissociated acetic acid as substrate (though not obligatory for all organisms) and unionized ammonia as inhibitor. The model also incorporates all important chemical species and activity coefficients in the equilibrium chemistry module (such as the phosphate buffer), resulting in more accurate pH predictions which is crucial for proper modeling of CO₂ and NH₃ stripping. This model can now be used to simulate processes that are operated under conditions where free ammonia inhibition can be an important factor for process efficiency and substrate conversions.

KEYWORDS

Anaerobic digestion, modeling, ADM1, ASDM, ammonia inhibition, acetate oxidation, ACOX

INTRODUCTION

Fig.1. The anaerobic model as implemented including biochemical processes: (1) acidogenesis from sugars, (2) acidogenesis from amino acids, (3) acetogenesis from LCFA, (4) acetogenesis from propionate, (5) acetogenesis from butyrate and valerate, (6) aceticlastic methanogenesis, and (7) hydrogenotrophic methanogenesis (Batstone et al., 2002)
Anaerobic digestion is a widely used and sustainable technology for treatment of various sludges and highly concentrated wastes. The metabolic pathways in anaerobic digestion are well known (Pavlosthatis, 1991). A standardized model based on research based models was published as the ADM1 in 2002 (Batstone et al, 2002). Another widely used model is the anaerobic digester model part of the General Activated Sludge – Anaerobic Digestion (ASDM) model (Comeau and Takacs, 2008) implemented in BioWin. The ASDM is targeted specifically at mesophilic anaerobic digestion of primary and waste sludges. The ADM1 is targeted at a wider range of applications, including higher temperature operation, and high-rate anaerobic treatment of industrial wastewaters. It is somewhat compromised in application to domestic sewage applications, which is its primary market.

As every model, both selected models contain simplifications resulting in certain deficiencies from an engineering perspective: The ADM1 a) requires parameter changes to represent differences in primary and waste sludge digestion (this was addressed by Nopens et al., 2006), b) has a non-intuitive input set that needs complex characterization or an input model, c) does not contain the phosphate buffer and e) does not consider precipitation. The ASDM does not contain an ammonia inhibition term foracetoclastic biomass. ASDM simplifies particulate substrate degradation and hydrolysis processes so the model can be used easier in practice in conjunction with existing activated sludge models and waste stream characterization techniques. Neither model contains the acetate oxidation mechanism which is the primary biochemical pathway under highly loaded, high ammonia conditions for the acetate degradation.

Anaerobic digester modeling on its own is less widespread compared to nutrient removal modeling due to fewer sludge digester configurations used in plants. However, the importance of digestion models that are valid under a wide range of operating conditions increases when the whole plant is considered in the context of plant-wide or within the fence modeling. The current paper discusses modifications which removes the limitations of existing digester models or extends their range of applicability, respectively.

**APPROACH**

- **Ammonia inhibition impacts on digestion modeling**

Mesophilic sludge digestion systems typically do not experience ammonia inhibition as long as no additional dewatering measures are taken (typical TSS-range of 4-6 % in the feed). In high-solids digestion systems (organic solid waste digestion or sludge digestion systems using pre-treatment processes) the ammonia concentration can exceed the toxic ammonia level of about 2500 mg NH₄-N/L. At this concentration level and corresponding alkaline pH the free ammonia produces an inhibiting impact on methanogenic growth (Angelidaki et al., 1993).

Fig. 2. Process scheme via acetate oxidation (ACOX): Toxicity impacts from ammonia release slows down the main route of acetoclastic methanogenesis and can cause a shift towards the metabolic alternative of acetate oxidation and consecutive hydrogenotrophic methanogenesis.
Free ammonia toxicity causes a bottleneck in the syntrophic process chain of anaerobic digestion (Fig. 2). In case of ammonia inhibition of aceticlastic methanogenesis a metabolic side-route over acetate oxidation to $H_2$ can become dominant. This adaptation process on microbial community level has been observed earlier (Karakashev et al., 2006; Wilson, 2009) and also the significance for a complete modeling approach has been outlined (Batstone et al., 2002) but so far it has not been implemented. Compared to ADM1 the ACOX model approach suggests following improvements:

- ACOX adds important missing degradation pathways so high loaded and high temperature anaerobic systems can also be simulated without recalibration of the model parameters;
- ACOX relates metabolic activity to unionised species such as undissociated acetic acid as substrate (though not obligatory for all organisms) and unionized ammonia as inhibitor;
- ACOX incorporates all important chemical species and activity coefficients in the equilibrium chemistry module (such as the phosphate buffer), resulting in more accurate pH predictions which is crucial for proper modeling of $CO_2$ and $NH_3$ stripping.

RESULTS AND DISCUSSION

Calibration of ammonia inhibition on aceticlastic methanogens and acetate oxidisers

Samples of biomass adjusted to high ammonia concentrations have been taken from a continuous bench-scale digester for thermally hydrolysed sludge (THD) and from a parallel conventional sludge digester (MAD). Then ammonia concentration was stepwise diluted and accumulative gas production was measured from batch-bottles (Wilson, 2009). Initial slopes of cumulative biogas production curves were used to determine the degree of inhibition imposed by unionized ammonia. These data are plotted as the fraction of biogas production activity remaining versus the concentration of unionized ammonia. For example, a reduction in the biogas generation rate by 20% would be plotted as an inhibition factor ($INH_3$) of 0.80, thus a high INH3 value (i.e. close to 1.0) would be indicative of little methanogenic inhibition. Previous research shows that ammonia inhibition of aceticlastic methane generation is relatively mild at low unionized ammonia concentrations and follows a logistic reduction in methanogenesis as ammonia is increased, theoretically leading to full inhibition of methanogenesis at sufficiently high concentrations (Angelidaki and Ahring, 1994). As such, the following logistic model has been applied to calculated $LI_{NH_3}$ values via least-squares regression (Wett et al., 2009):

$$LI_{NH_3} = \frac{1}{1 + e^{-(slope_{I,NH_3})(k_{I,NH_3}-(NH_3))}}$$

Eq. 1)

where $slope_{I,NH_3}$ is a curve fitting parameter, and $k_{I,NH_3}$ is the molar unionized ammonia concentration at which $INH_3 = 0.50$.

Methanogenic inhibition factors (INH3) related to the initial slope of cumulative biogas production curves from batch ammonia toxicity assays are presented in Figure 3. The logistic inhibition function Eq.1) was calibrated to the parameters given in Table 1. It is clear that the degree of methanogenic inhibition attributable to NH3 is less for THD than MAD at equivalent NH3 concentrations. The logistic model that was applied to these data exhibited good statistical fit. Coefficients of determination ($R^2$) of $LINH3$ for THD and MAD were 0.947 and 0.951, respectively. The relative insensitivity of the THD culture to free ammonia inhibition relative to the MAD culture becomes particularly pronounced as the free ammonia concentration exceeds 150 mg/L N. It is thus hypothesized that methanogenesis during THD is less dependent on ammonia-sensitive aceticlastic methanogenesis, and rather, non-aceticlastic methanogenesis from HAc is important for THD.
Fig. 3. Inhibition factors ($I_{\text{NH}_3}$) related to the measured initial slope of cumulative methane production from batch ammonia toxicity assays using sludge from a mesophilic digester (MAD) and a thermal hydrolysis digestion system (THD) and fitted model profiles.

Tab. 1. Calibrated parameters for ammonia inhibition of growth of aceticlastic methanogens and acetate oxidizers

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**Population shift at increasing ammonia concentrations at CAMBI pilot at Blue Plains**

An archaeal clone library was constructed from digested biosolids from pilot-scale anaerobic digestion systems treating raw and thermally hydrolyzed combined (primary and secondary) wastewater sludge. In total, 161 genomic DNA inserts (88 from thermally hydrolyzed biosolids, 73 from raw biosolids) were recovered from successful clones. Data from highly similar sequences (greater than 99% sequence similarity) were defined as operational taxonomic units (OTUs). Each sequence was searched for phylogenetic relatives using the nucleotide BLAST (BLASTn) program (Altschul et al., 1990).

For anaerobic digestion of conventional sludge (MAD), methanogens belonging to OTUs having greater than 99% similarity to *Methanosarcina barkeri* dominated (66% of total clones). The minority population closely matched an uncultured *Methanomicrobiales* archaeon (97% similar to *Methanospirillum hungateii*, approximately 22% of clones). It is thought that this methanogenic population structure reveals a preference for aceticlastic methanogenesis (direct acetate cleavage) rather than acetate oxidation (via hydrogen as an intermediate). On the contrary, the digester treating thermally hydrolyzed sludge (THD) was dominated by hydrogenotrophic *Methanocellus bourgensis* (100% similarity) at 77% of total clones. The remainder of this methanogenic community consisted of near equal ratios of hydrogenotrophic *Methanospirillum hungateii* (97% similarity, 10% of library) and aceticlastic *Methanosarcina sp.* (100% similarity, 13% of library). It is apparent from these data that high solids anaerobic digestion of thermally hydrolyzed sludge results in selective pressure for the growth of hydrogenotrophic methanogens relative to aceticlastic methanogens. Both functional groups of acetate consumers (cleaver and oxidizer) are more sensitive to ammonia relative to hydrogenotrophic methanogens, but acetate cleavers are most. It is presumed that this selective pressure is due to the channeling of acetic acid through a non-
aceticlastic pathway, thus producing additional hydrogen and carbon dioxide as methanogenic substrates. These experimental data are shown in Figure 4 (left). Applying the described model ACOX which incorporates acetate oxidation under high unionized ammonia (i.e. high solids) concentrations, a similar shift towards hydrogenotrophic methanogenesis is observed (Figure 4, right).

**Fig.4.** Fractions of methanogenic organisms (percentage of total methanogenic population) grouped by primary substrate methane and hydrogen – based on phylogenetic measurements (left; from Wilson, 2009) and model simulations (right)

**Steady state validation run – varying solids concentration at CAMBI pilot at Welsh Water**
CAMBI pilot tests have been conducted by Wesh Water to mimic variations of total dried solids (DS) concentration in the digester feed at constant load. The corresponding SRT-variation was between 14.7 and 15.8 days. Validation runs of the ACOX model could match the more pronounced VFA increase at DS concentrations in the feed exceeding 9% solids (Fig.5).

**Fig.5.** Measured (Welsh Water CAMBI pilot) and simulated acetate response to varying feed solids concentrations (sludge characteristics of Blue Plains)

**Dynamic validation run – start-up of CAMBI digestion at Oxley Creek**
Oxley Creek has a Cambi Thermal hydrolysis unit feeding two 2600 m$^3$ anaerobic digesters. Only data from digester 1 is presented here, but a similar response was observed in digester 2 (Batstone et al., 2010). As digester load was ramped up (Fig. 6a), the ammonia concentration increased (Fig. 6b). As it passed through 0.008M ammonia as NH$_3$, an acute response in acetate concentration up
to 2500 mg/L was observed. This was initially managed by reducing load to the digester, but eventually took 30 days to decrease fully to background levels (approx. 300 mg L$^{-1}$). The digesters have remained at this level since for over 3 years. The retention time at the point of overload was 22-25 days, and input solids concentration approximately 9%. During start-up of the 2nd digester acetate peaked up to about 4500 mg/L and was degraded even at continued ramp-up of load.

![Graph](image)

**Fig. 6.** Measured profiles of total and volatile solids (6a-top) and ammonia and acetate (6b-bottom) during start-up (100 days) of the CAMBI-digesters in Brisbane (from Batstone et al., 2010)

A similar initial ramp-up of digester load was applied by the model resulting similar responses in digester solids built-up (Fig.7a) and acetate peak (Fig.7b) although again the influent characterization of Blue Plains (and not Oxley Creek) was used. The main difference regards the final acetate level at constant load. The measured acetate effluent concentration was unusual low compared to all other CAMBI-data sets under investigation and also compared to the model result. This fact can be explained by a lower observed pH-level of about 7.55 compared to 7.85 meaning a free ammonia concentration of about 125 compared to 225 mg N/L in the modeled scenario. Spot samples of Oxley Creek THD sludge showed high abundance of *Methanosarcina* indicating acetate oxidation as the main metabolic route. However this does not mean a complete wash-out of *Methanosaeta* as predicted for a model environment at ideally homogenous conditions (compare Fig.4). *Methanosaeta* as the main acetate cleaver is usually seen in environments with low VFA levels.
Fig. 7. Simulated increase in digester solids concentration (7a-top) and ammonia concentration and corresponding acetate accumulation and degradation (7b-bottom) due to a shift of metabolic pathways towards acetate oxidation during digester start-up period of 100 days (5% feed-flow increase per day; sludge characteristics of Blue Plains).

Fig. 8. Population dynamics of aceticlastic methanogens, acetate oxidizers (user defined3) and hydrogenotrophic methanogens in response to increasing ammonia inhibition.

**Generic model applicability to a broad range of digester types**

The described model approach has been applied to simulate four types of anaerobic processes in order to demonstrate the range of applicability. A short summary of the main variables of these digesters operated at different SRT and temperature is given in Table 2.
<table>
<thead>
<tr>
<th>Tab.2. Modelled biomass compositions over a range of systems</th>
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<tbody>
<tr>
<td>Units</td>
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<td>-----------------</td>
</tr>
<tr>
<td>SRT days</td>
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<td>Temperature C°</td>
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<td>Input TDS %</td>
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<td>pH</td>
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<td>VSR %</td>
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<tr>
<td>VFA mgCOD/L</td>
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<tr>
<td>NH3 mgN/L</td>
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<tr>
<td>Fermenting organ. %</td>
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<tr>
<td>Acetogens %</td>
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<tr>
<td>Aceticlastic meth. %</td>
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<tr>
<td>Acetate oxidizers %</td>
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<tr>
<td>Hydrogenotrophs %</td>
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</tbody>
</table>

CONCLUSIONS

The current versions of anaerobic digestion models (ADM and ASDM) are unsuitable when highly loaded conditions or high temperature digestion processes need to be considered. The authors have proposed a model modification that allows for the use of free ammonia tolerant acetate oxidation pathway under ammonia inhibiting conditions using a logistic free ammonia inhibition function for the aceticlastic and acetate oxidizers. This modification to existing models helps to mimic dynamic adaptation to a toxic process environment by a shift between different sensitive populations, to accommodate these high loaded and high temperature anaerobic systems without artificially recalibrating the model parameters. The model also relates metabolic activity to unionised species such as undissociated acetic acid as substrate (though not obligatory for all organisms) and unionized ammonia as inhibitor. Inhibition values have been estimated for this model to simulate thermophilic digestion and highly loaded mesophilic digestion processes. This is a significant improvement that allows for anaerobic digestion to be used by practitioners wanting to employ and evaluate these types of processes for design, upgrade or operations.

REFERENCES


There is an increased interest in enhancing biogas production in existing anaerobic digesters by co-digesting treatment plant sludge with other organic materials (Zitomer et al., 2008, Schaefer et al., 2008, Kabouris et al., 2007). Codigestion can provide significant advantages to plant operations by enhancing energy recovery, reducing greenhouse gas emissions and add revenue from tipping fees. Codigestion can also add to the amount of sludge to be disposed and increase the loading rates to the liquid treatment train from dewatering operations and impact the quality of the biogas for treatment and create toxicity impacts that can challenge digestion operations. (Zitomer et al., 2008).

Adequate quantification of enhanced biogas production and biogas quality, final sludge to be disposed and changes in return loads is of importance when evaluating the overall costs and benefits of codigestion. Anaerobic Digestion Model number 1, AD1, is usually employed to quantify the performance of Digestion of Sludge. Significant efforts to integrate AD1 with liquid train treatment models to obtain plant-wide models, e.g. activated sludge models ASM-AD, are currently underway (Nopens et al., 2009, Zaher et al., 2009)). Codigestion models are usually composed of an AD engine, e.g. AD1, a set of transformers for translating codigestion material characteristics to AD model inputs, and hydrolysis models. These parts are then combined into a way that the AD engine can accept as input. This paper provides a state of the art review of current practice for modeling codigestion of organic substrates at WWTP including the different components previously mentioned. It will critically review existing AD models, model transformers and interfaces, and requirements for modeling hydrolysis of different materials. It will provide an identification of modeling needs and the evaluation of alternative proposals in the literature for dealing with perceived deficiencies. In particular the following aspects
will be review in detail: Synergistic and Antagonistic effects of codigestion, Impact of codigestion materials on alkalinity and pH modeling needs, Impact of codigestion materials on biogas composition e.g. hydrogen sulfide, Alternative expressions for hydrolysis modeling, calculation of dewatering liquors compositions (estimation of return loads for plant treatment), use of common laboratory test e.g. BMP for characterizing codigestion substrates. An example relating modeling of synergistic and antagonistic effects is presented below.

**Modeling Synergistic and Antagonistic Effects**

Zitomer et al. and Kabouris et al., have reported enhancements in the methane yield of substrates during laboratory anaerobic co-digestion tests (Zitomer, et al., 2008, Kabouris et al., 2008). In some cases the observed enhancement in methane yield is beyond what would be possible from a COD mass balance (Zitomer et.al., 2008). Also several researchers have reported reduction in plant sludge dry solids after co-digestion with fats, oil and grease, FOG. Kabouris also suggested that some of the procedures used for analysis of codigestion biochemical methane potential tests, BMP, would need to be revised due to potential synergistic co-digestion effects. This contribution focuses in incorporating synergistic biodegradation effects in mathematical model of anaerobic co-digestion.

**Model**

We programmed AD1 equations to track in a steady state condition the biodegradation of a complex material. The impact of bacterial growth and degradation and inert components were carefully included as they impact methane yield. Composition of the material was obtained using Zaher procedures (Zaher et al., 2009). An example of the output of the model for different fractions of the digestion process as a function of SRT is presented below:
We include independent biodegradable fractions when co-digesting different materials. In this way the impact of one substrate on the biodegradability of the other can be independently obtained. Two independent equations are obtained and can be solved simultaneously based on data obtained during a BMP test. All mathematical development will be presented.

An example of the additive model and the synergistic model of biodegradation is presented below:

It is observed that the additive model under-predicts the actual biodegradation of FOG during BMP tests. As a result the methane yield for FOG is overestimated producing
inconsistent results in the COD balance. At the same time biodegradation of sludge is under-predicted as presented in the graph below:

The impacts of changes in biodegradability as a result of synergistic effects are significant: methane production during full-scale co-digestion can be underpredicted and sludge production over-predicted. This in turn significantly affects the economic evaluation of a codigestion project. An example of the application of the model in the FOG case is presented in the graph below:
It is clear that incorporating synergistic effects in the biodegradability of substrates is important for accurate evaluation of codigestion projects. The economic implications will be discussed. Recommendations for improved protocols for characterization of co-digestion materials will also be presented. Analysis methods for BMP data will be discussed. A second set of data for organic fraction of municipal solid waste codigestion will also be presented.

REFERENCES


