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Review

Mathematical modelling of anaerobic reactors treating domestic wastewater: Rational criteria for model use

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Abstract

Anaerobic digestion modelling is an established method for assessing anaerobic wastewater treatment for design, systems analysis, operational analysis, and control. Anaerobic treatment of domestic wastewater is a relatively new, but rapidly maturing technology, especially in developing countries, where the combination of low cost, and moderate-good performance are particularly attractive. The key emerging technology is high-rate anaerobic treatment, particularly UASB reactors. Systems modelling can potentially offer a number of advantages to this field, and the key motivations for modelling have been identified as operational analysis, technology development, and model-based design. Design is particularly important, as it determines capital cost, a key motivation for implementers. Published modelling studies for anaerobic domestic sewage treatment are limited in number, but well directed at specific issues. Most have a low structural complexity, with first order kinetics, as compared to the more commonly used Monod kinetics. This review addresses the use of anaerobic models in general, application of models to domestic sewage systems, and evaluates future requirements for models that need to address the key motivations of operational analysis, technology development, and model-based design. For operational analysis and technology development, a complex model such as the ADM1 is recommended, with further extensions as required to address factors such as sulphate reduction. For design, the critical issues are hydraulics and particles (i.e., biomass and solid substrate) modelling. Therefore, the kinetic structure should be relatively simple (at least two-step), but the hydraulic and particulate model should be relatively complex.

1. Introduction

Modelling of anaerobic wastewater treatment is a mature research and application field, now in its third generation, and with a strong push towards standardisation of model structure and parameters (Batstone et al. 2002). Despite this, anaerobic digestion is one of the only key biological processes in wastewater treatment that does not generally use a non-linear kinetic model for design. Instead, anaerobic digesters are most often designed on a combination of hydraulic and COD mass loading. In contrast, activated sludge biological nutrient and COD removal designs are often based on the ASM1 (Henze et al. 1987), even though the kinetics may be simplified to zeroth order. There are several reasons for this:

(a) Parameters for anaerobic digestion have not been well estimated or standardised (Batstone et al. 2002), and assessment of parameter variability is limited.
(b) The most popular anaerobic models currently are very complex, and the information contained in parameter values and model structure does not translate well to simple design rules.
(c) Wastewater design reference texts are often written with a strong bias towards activated sludge processes (Tchobanoglous & Burton 1991; Henze et al. 2002), and this theme

impacts the anaerobic design chapters. While this is reasonable – readers need a common basis, it has lead to less relevant concepts, such as sludge age, and growth rate – being applied in a sub optimal way to anaerobic digestion.

(d) Classic design of anaerobic processes is concentrated on design of primary sludge digesters. These are very different processes from low concentration units such as anaerobic domestic sewage treatment systems.

However, modelling offers some very real advantages in design and analysis applications, especially for anaerobic sewage treatment process design. Concentrations are relatively low, which means that kinetics are near or below K_S values, and are therefore non-linear. Also, the advanced gas–liquid models in many current anaerobic digestion models are very well suited for modelling residual levels of COD caused by limited gas stripping at low concentrations.

The importance of modelling was recognised by Seghezzo et al. (1998) in a review of anaerobic sewage treatment by UASB reactors. The authors identified accumulation and conversion of suspended solids as a key factor, and proposed mathematical modelling as a key tool for management of sludge inventory (both substrate and biomass) within the reactor.

An important part of modelling is assessing motivation for applying a model. Without a clear set of objectives, modelling will not give reasonable outcomes, and model design specifications are fuzzy. Common motivations, applications and model requirements are shown in Table 1. This is discussed further in the first part of section 4, but briefly, the key motivations for modelling of anaerobic domestic sewage treatment are probably operational analysis, technology development, and model-based design.

This review outlines current knowledge, and requirements for future modelling of anaerobic domestic wastewater treatment. The principal elements of an anaerobic digestion model are given in Section 2. Current application of models to anaerobic digestion of domestic wastewater is reviewed in Section 3. In Section 4, methods to build models for the three main motivations of operational analysis, technology development, and model-based design are proposed.

2. Mathematical modelling of anaerobic systems

The types of biochemical models used in anaerobic systems are, from least to most complex; steady state models, one and two step dynamic models, and fully structured dynamic models. Additionally, these can be used in hydraulic or biofilm models with varying degrees of complexity. Also of high importance in anaerobic digestion models are the physicochemical models, which are to assess gas transfer and (optionally), pH. All models of anaerobic processes need a physicochemical component in order to predict gas flow, but use of more complex models allows prediction of more factors.

2.1. *Basic elements of anaerobic models*

2.1.1. *Mass balances*

The basis of all mathematical models is a mass balance for a specific state variable. This describes accumulation and reaction within a system in relation to flow across the system boundaries (Figure 1, Eq. 1) or mathematically:

$$\frac{dM_{\text{sys}}}{dt} = m_{\text{in}} - m_{\text{out}} + r \tag{2}$$

where M_{sys} is the mass in the system (units mass), m_{in} and m_{out} are the mass flow rates in and out (units mass×time^{-1}), and r is the overall generation rate (units mass×time^{-1}). The overall generation rate is a sum of all the different rates influencing the compound being modelled ($r = \sum_n \rho_i$, where $\rho_{1\ldots n}$ are the different conversion rates).

Most anaerobic systems (even sludge digesters) are dilute systems, and concentration changes have no impact on volume. If the reactor is well mixed, the concentration of a component in a stream out of the reactor is the same as that within the reactor. Therefore, Eq. 2 can be expressed as follows over the whole reactor:

$$\frac{dVC_{\text{sys}}}{dt} = q_{\text{in}}C - q_{\text{out}}C_{\text{sys}} + Vr_{\text{c}} \tag{3}$$

where V is the volume of the reactor, C is the concentration of a component and r_{c} is the over-

all generation rate of component ***C*** (negative if consumed).

At steady state, the accumulation term is zero, and the differential equations become a set of algebraic equations that can be solved for C_{sys}. This is the basis of for static design methods used by popular text books (Tchobanoglous & Burton 1991; Henze et al. 2002). An explicit solution for C_{sys} is only possible for simple models with 1–2 microbial groups and related substrates. As more microbial compounds, and other factors such as gas–liquid transfer are added, the algebraic set of equations becomes non-linear, and may result in multiple solutions.

2.1.2. *Kinetics*

A critical part of the mass balance is the rate equation (rc), as the other terms are fixed by hydraulics. There are a wide range of kinetic relationships used (Pavlostathis & Giraldo-Gomez 1991), but the most popular relationship to describe biological activity is the Monod (or Michaelis–Menton) kinetic:

$$\rho = k_m \frac{S}{K_s + S} X \tag{4}$$

This can be modified to include a wide range of inhibition and regulation mechanisms as required:

Table 1. Anaerobic digestion applications and motivations

Motivation	Application	Technical considerations
Model-based analysis and improvement of existing systems (operational analysis)	An existing system for which parameters can be tuned, and which may have specific limitations.	Required data can be sourced directly. Parameters can be optimised specifically for that process. Model needs to include limiting or controlling mechanisms.
Model-based design	Design of new, full-scale systems.	Model needs to be accessible, and standardised. Need very good parameter sets. Need to consider hydraulics and particle behaviour.
Technology development	Development of new technology either using only models, or using models to assess technology.	Model needs factual, fundamental basis.
Parameter estimation	Estimation of transportable parameters for other applications and design.	Good parameter estimation procedure. Highly defined model. Identifiable model (or key process).
Integrated system analysis	Process selection, process justification.	Anaerobic model needs to interact with other models. Models should be adequate to answer selection/design questions.
Sensor analysis	Analysis of respirometric sensors.	Needs to include underlying processes, for respirometric sensor (and generally also physicochemical processes).
Model-based control	Non-linear control of systems.	Minimalist model that properly models behaviour of critical inputs and outputs.
Control and operation system benchmarking	Testing of new strategies.	Need complicated and realistic model.

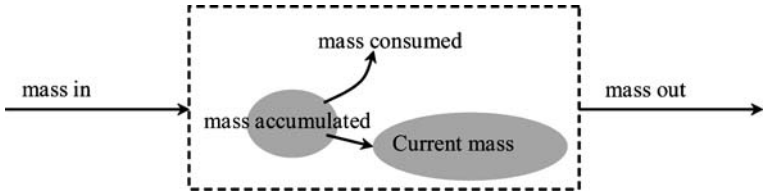

Figure 1. Mass balance and system boundaries.

$$\rho = k_{\mathrm{m}} \frac{S}{K_s + S} X \times I_1 I_2 \ldots I_n \qquad (5)$$

where inhibition mechanisms can include classic non-competitive inhibition, empirical inhibition mechanisms, or competitive terms. Other inhibition mechanisms, such as uncompetitive, or competitive require modification of the Monod term (Eq. 4) (Pavlostathis & Giraldo-Gomez 1991).

2.1.3. *Physicochemical components*

The basic elements of the physicochemical system are gas flow calculation, and pH calculation. All methanogenic anaerobic models need to describe gas flow in some form, though fermentative or preferementer models may not (von Munch et al. 1999). Complicated, structural models generally also include pH calculation because of its strong impact on carbondioxide transfer and mineral solids precipitation, and biological conversions (Costello et al. 1991; Angelidaki et al. 1999; Batstone et al. 2002; Siegrist et al. 2002).

2.1.3.1. *Gas flow calculation*. There are several methods of calculating gas flow in a model, from least to most complicated:

(a) Assume a fixed gas concentration, and calculate total gas flow from COD conversion across the system. This is often used with very simple models and fails in prediction outside steady state conditions.
(b) Calculation of individual gas production from either two-film gas–liquid transfer theory (Batstone et al. 2002) or assuming equilibrium. Set total gas flow equal to sum of individual production rates.
(c) Same as for (b), except set gas flow using a pressure differential between headspace and atmosphere.

Both methods (b) and (c) require modelling of the headspace as a vessel (generally with fixed volume). Method (c) is slightly more complicated than method (b), and was originally implemented to negotiate limitations in specific modelling packages. However, it has since been found to be more numerically stable, as (b) can result in multiple steady state solutions.

2.1.3.2. *Acid–base equilibria*. Models of anaerobic digestion have classically included comprehensive, accurate pH predictive systems. pH calculation involves solving a set of algebraic or differential equations to calculate the concentrations of ionic acids and bases related with ionic, active concentration state variables. There are a number of methods of both formulating and solving the related equations, using both differential, and algebraic numerical solvers (Stumm & Morgan 1996; Musvoto et al. 2000b; Batstone et al. 2002; Siegrist et al. 2002). Though more complicated, the methods used in anaerobic digestion modelling are more comprehensive and informative than tracking a generalised alkalinity variable, as often used in aerobic models (Henze et al. 1987). Commercial aerobic models are therefore starting to include comprehensive pH prediction.

2.1.4. *Biochemical structure*

The sub-processes in anaerobic digestion are well known, and have been extensively evaluated in a number of reviews (Gujer & Zehnder 1983; Pavlostathis & Giraldo-Gomez 1991; Batstone et al. 2002). Briefly, the processes include: (a) Extracellular *hydrolysis* of particulates to monomers, (b) *acidogenesis*, or fermentation of monomers to alcohols, bicarbonate, hydrogen and organic acids, (c) *acetogenesis*, or oxidation of alcohols and organic acids to hydrogen and acetate and (d) *methogenesis* from hydrogen and acetate.

Methanogenesis is actually 2 parallel processes; aceticlastic and hydrogenotrophic methanogenesis.

Knowledge about individual processes varies. For hydrolysis, individual mechanisms are well known, but because of variation in substrate chemical and physical properties, the entire complicated processes are often lumped as a single, first order process (Eastman & Ferguson 1981; Pavlostathis & Giraldo-Gomez 1991). It is very difficult to justify complicated kinetics (Vavilin et al. 1996), except when dealing with pure substrates (Sanders et al. 2000).

Stoichiometric pathways for protein fermentation have been proposed, based on Stickland fermentation (Ramsay & Pullammanappallil 2001). However, the authors of this study found oxidative pathways occurring more than expected, perhaps due to low concentrations of hydrogen. Individual pathways for glucose fermentation are also well characterised in pure culture (Madigan et al. 2000), and there are approximately four commonly recognised stoichiometric pathways to butyrate, acetate, ethanol + acetate, and propionate + acetate (Ren et al. 1997; Batstone et al. 2002). In each pathway, excess electrons are wasted to hydrogen, and carbon to bicarbonate. There is also a proposed intermediate pathway to lactate (Costello et al. 1991). However, despite a number of proposed regulation mechanisms (Mosey 1983; Costello et al. 1991; Ruzicka 1996), glucose acidogenesis models are still not effective. This limitation is becoming critical, as fermentative hydrogen production is now an intensively researched technology for energy production.

The microbial populations, as well as governing mechanisms are well described for acetogens (Schink 1997; Hansen et al. 1999), and both groups of methanogens (Ferry 1993). Models including these processes are only limited by full characterisation of kinetic rates (Batstone et al. 2002), and inhibition factors such as hydrogen, free ammonia, and pH inhibition. This is improving, with specific studies directed towards these factors (Siegrist et al. 2002; Batstone et al. 2003).

2.1.4.1. *Rate limiting steps*. The two slowest steps in the process are often Hydrolysis, or Aceticlastic Methanogenesis (Pavlostathis & Giraldo-Gomez 1991). In systems with high solids, such as primary or activated sludge digesters, overall system efficiency is often defined by hydrolysis rate, and extent (Gossett & Belser 1982; Pavlostathis & Gossett 1986, 1988). This can determine whether a large structured model, or simple, first order model is necessary to adequately define the system. However, different limitations can impact different key steps. This, as well as advances in model accessibility and computing power have caused most current models to become complex, structured models.

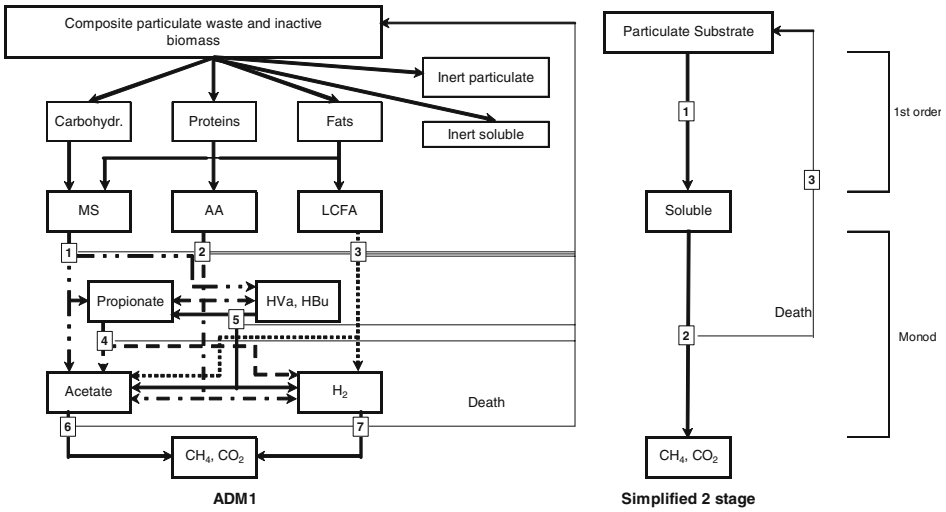

Figure 2. Alternative model structures. ADM1 contains 19 processes, and 26 state variables. Simplified 2 step contains three processes (hydrolysis, uptake, decay) and 3–4 state variables (particulate substrate, soluble substrate, biomass, optional biogas).

2.2. *Model application*

Modeling of anaerobic digestion has expanded heavily in the last 20 years, with a development towards more complicated biochemical structures (e.g., ADM1, Figure 2). Early models were single stage kinetic (Pavlostathis & Gossett 1986) and orientated on homogeneous, but complicated substrates such as activated sludge. The single stage models were often used for evaluating biodegradability and gas flow at steady state. The most important parameter (particularly for activated sludge) is probably biodegradability, which is not a kinetic parameter (Gossett & Belser 1982).

Structured models were implemented to simulate particular factors such as organic acid accumulation. In particular, inclusion of pH prediction through physicochemical equations requires a complex biochemical structure. Structural models have been generally orientated towards specific applications, such as: Manure/oil codigestion (Angelidaki et al. 1999), with focus on ammonia and long chain fatty acid inhibition, two stage high-rate (Costello et al. 1991; Batstone et al. 2000), municipal sewage sludge (Siegrist et al. 1993, 2002), general use, though oriented toward particulate material (Vavilin et al. 1994) and glucose (Kalyuzhnyi & Davlyatshina 1997). Although most of the models were oriented towards a specific wastewater type or reactor design, the basic structure was similar, with hydrolysis, acidogenesis, acetogenesis, and methanogenesis steps. This was motivation for formulation of the ADM1 (Batstone et al. 2002), which aims to unify the main models, and facilitate research into areas apart from general structure.

While complex model structures are ideal for complex process analysis, much simpler model structures may be required for design and hydraulic analysis (see Section 4). Other applications such as model-based process control require a minimalist, model, with defined structural elements (Bernard et al. 2001).

3. Models for anaerobic domestic wastewater treatment

3.1. *Models for complex wastewater*

Apart from structure, the biggest differences in published models is in hydraulic implementation, but this will depend on specific implementation, and is discussed further in the next section. In this section, suitable model structures for domestic wastewater are discussed.

Referring the previous section, there are essentially three classes of models:

(a) Exclusive; or those that model a single, rate-determining step, and are therefore very simple.
(b) Minimalist; those that model the minimum number of steps required for a specific purpose. These mainly encompass control models such as (Bernard et al. 2001) or instrument development.
(c) Inclusive; those that include all processes and components found in a specific, or even complex wastewater. This category can also include simplified inclusive models, in which several steps have been lumped. This is separate from minimalist, since the structure of minimalist models is often based on numerical considerations.

Exclusive model structures are basically identical, as they all contain a single first order, or Monod kinetic. They are suitable for specific applications in domestic wastewater as discussed further.

Minimalist models are mostly suitable for specific analytical applications that are not yet applied to anaerobic domestic wastewater treatment, and are not a priority due to buffering and low loading rates (see Section 4).

Inclusive models are also effectively very similar, as discussed in the previous section. However, because of basis, application, and parameters, there are two in particular that are suitable for wastewater treatment applications. The ADM1 (Batstone et al. 2002) is a standardised, inclusive model that uses a COD basis, with most of the outputs that are required for anaerobic domestic wastewater treatment applications. Sulphate reduction is possibly an additional requirement. Because it is standardised, it is easier to source parameters, and the default parameters give reasonable results when applied anaerobic domestic wastewater treatment, though they may need adjustment for low temperature conditions. It is also available in a range of modelling package (contact authors for details). The Siegrist model (Siegrist et al. 1993, 2002) is a very popular model for describing degradation of

primary sewage sludge. It is very comparable to the ADM1, with omission of butyrate and valerate from the Siegrist model, and implementation of hydrolysis as a single step. The parameters from Siegrist are also comparable with the parameters in the ADM1, with a higher effective decay rate, but also higher uptake rate (the two are correlated). The parameters from Siegrist et al. (2002) are based on experiments, while those from Batstone et al. (2002) are based on review consensus. Either of these structures and parameter sets can be used for domestic anaerobic wastewater treatment modelling.

3.2. *Models applied to domestic wastewater*

Anaerobic treatment of domestic wastewater is an emerging field, and application of models limited compared to primary, activated sludge, and industrial wastewaters. It has benefited from the previous work in this field, and despite the short period of application, some advanced, and well targeted studies have been published (see below).

3.2.1. *Steady state 1st order and constant conversion*

The simplest models have been constant conversion steady state models (i.e., a specific fraction of COD is assumed to convert to biogas). These are best used for cost analysis, and integrated process analysis, and have generally been used as such. Because of implementation of the Kyoto protocol, integrated analysis of greenhouse gas generation (GHG) has increased in importance, and this has been used to assess GHG generation from different wastewater treatment plant configurations (Keller & Hartley 2003; Greenfield & Batstone 2005). Both these studies used a very simple single stage, fixed conversion model to assess contribution of renewable energy from anaerobic sewage, and sludge treatment within the context of different treatment plant configurations. Zakkour et al. (2001) used a more complicated study to assess conversion in a two-stage (hydrolytic and methanogenic) reactor system, with conversion efficiency related to operating temperature. This model also included kinetic elements, with a steady state implementation of first order kinetics for the hydrolysis tank. Liquid phase gas, was also included which can be very important (see later). Medri and Medri (2002) used a conversion efficiency, based on observed first order coefficients (at steady state) for comparative cost analysis of anaerobic stabilisation pond systems. A two-stage anaerobic pond system was recommended over a facultative pond system. Single step steady state kinetics of a combined anaerobic-aerobic system (Castillo et al. 1999) were used to compare biomass uptake rate models. Monod, first-order and zeroth order were compared. First order kinetics were statistically the best, compared to zeroth order. The kinetic parameters for Monod kinetic were over-correlated, indicating effective first order kinetics. Zaiat et al. (2000) assessed kinetics in horizontal flow reactors, using a complex hydraulic and (effective) biofilm model, with first order biological kinetics. This is a promising and unique combination of plug-flow and biofilm kinetics for assessing biofilm systems in non-CSTR hydraulic systems, and could also be applied to UASB systems.

3.2.2. *Dynamic implementation*

Toprak (1995) used a single step first order model in soluble COD to model a laboratory-scale anaerobic pond. The model was solved using the analytical solution of first order kinetics in a mixed-tank system. Measured data were used to estimate the impact on the first order coefficient (k) of a number of parameters, including temperature. Temperature dependence of kinetics, based on the Arrhenius equation was confirmed, compared to other studies (e.g., Zakkour et al. 2001). A similar approach was used in assessing an anaerobic sequencing batch reactor (Rodrigues et al. 2003). This model was again used to fit apparent first order coefficient, with residual, and used to assess feed time over cycle time. This model was expanded to two stage first order (Rodrigues et al. 2004) to predict organic acid concentrations. A limited subset of the ADM1 was applied to a two-stage upflow septic system (Elmitwalli et al. 2003). The two stages were hydrolysis, and biological growth (or uptake), with decay. The model results, with additional experimental data were used to evaluate the impact of temperature on design parameters, including hydraulic retention time.

3.2.3. *Observations: Classic modelling versus anaerobic sewage modelling work*
In comparison to "classic" anaerobic models, the published sewage models have several key features:

3.2.3.1. *Kinetics*. First order kinetics are much more popular than Monod kinetics. This is partly because there is no analytical solution to Monod kinetics under dynamic conditions. However, it is also a sensible approach at low substrate concentrations. Under these conditions, Monod kinetics approach first order kinetics. Published K_S values are generally above 100 g COD m^{-3} (Batstone et al. 2002, 2003; Siegrist et al. 2002) and quantitative parameter estimation in sewage systems has shown Monod is unidentifiable compared to 1st order (Castillo et al. 1999). However, I believe use of Monod is a better approach in the long term, and this is further discussed below.

3.2.3.2. *Model structure*. The objectives of the modelling work are often clearly outlined, and oriented towards design questions. This is actually a very good approach. Historical anaerobic modelling has generally focused on theoretical model presentation, and operational analysis. Given that capital costs are critical within the target market for anaerobic sewage systems (von Sperling 1996), this is understandable. This has emphasised the use of steady state models, and single step, first order kinetics. As operational considerations become more important (perhaps driven by effluent limits), structured, complex models may also become more important.

The next section will discuss the future of anaerobic modelling of sewage sludge, and likely directions for improvements, for design, operation, and theoretical analysis.

4. Views, outlook, and recommendations

4.1. *Current and future requirements*

It is evident that anaerobic treatment of domestic wastewater is now changing from emerging to established technology, having been widely applied in full-scale treatment. It is a particularly attractive option in developing countries, as it is cheap in terms of capital and operating costs, and is relatively simple to construct and operate, in comparison with competing activated sludge technologies (von Sperling 1996). From the literature reviewed, there are two main classes of anaerobic sewage treatment technologies applied. Low rate mainly encompass anaerobic stabilisation ponds, and are historically very popular. High-rate include upflow anaerobic sludge blanket (UASB), expanded granular sludge bed (EGSB), and other variants, including anaerobic baffled reactor (ABR), and anaerobic sequencing batch reactor (ASBR). The future probably lies with high-rate digesters, as stabilisation ponds suffer from high land usage, and high environmental impacts (sight, odour, and effluent), as well as difficulty in effective design. Among the high-rate technologies, the UASB will probably dominate, with significant competition from ABR and ASBR reactors. ABR reactors particularly have strong advantages for good effluent quality (Barber & Stuckey 1999), partly because of semi-plug flow kinetics. ASBR reactors have similar advantages, though high substrate conversion rates are driven by concentration variations in time, rather than space. Both ABR and ASBR are higher cost than UASB. The opinions in this section will chiefly concentrate on high-rate digestion, with special emphasis on UASB technology.

Among the typical applications evaluated in Table 1, the applications so far have concentrated on integrated analysis, and design (mainly acquisition of design parameters). These will continue to be important, and design in particular is critical, as it has a strong impact on capital cost. Another observation is that many of the studies have concentrated on relating the primary design parameter (apparent first order kinetic constant) with temperature, which has an analogue with nitrification design in activated sludge (Henze et al. 2002).

While design will continue to be important, operational and technology issues threaten long-term environmental sustainability of anaerobic sewage treatment. These include (in nominal order of importance):

(a) odour and gas utility problems due to the presence of sulphides
(b) relatively high effluent COD (especially periodically)

(c) reactor stability (related to (b))
(d) inadequate nitrogen and phosphorous removal
(e) loss of product (methane), and greenhouse gas (GHG) impacts due to methane solubility

Startup is also a possible concern, but is greatly alleviated by use of a suitable inoculum.

GHG production and release is of low importance to the target market (the global and local impact of wastewater-related GHG release in developing nations is low), but the Kyoto protocols specifically address technology transfer, and GHG reduction in Non-Annex 1 countries by technology transfer and funding mechanisms. This is likely to provide a strong motivational force for methane recovery technology in developing nations, and such projects are already occurring (Cohen & Clarke 2004), with additional economic benefits.

Among concerns in the list above, (b), and (c) are related to operational analysis. The other issues can only be resolved by developing new technology. The technology basics are already known; and often with a well-characterised biological basis (e.g., a:sulphate reduction or sulphide oxidation, d:nitrification). In other cases, physicochemical factors dominate (e.g., e:gas stripping), which are a core part of anaerobic digestion modelling.

In summary, the three critical applications are as follows: (a) Design: acquisition of design par ameters and laws; (b) Operation: optimisation of reactor stability, and prediction of undesirably by-product release (COD, nutrient, and gases); (c) Technology development: develop new technology to further develop long-term sustainability of anaerobic sewage treatment. The rest of this section will address model components with respect to these applications.

4.2. *Biochemical structure and kinetics*

Biochemical model structure requirements are different for design, and operation/technology development. A simplified model structure (Elmitwalli et al. 2003) (recommended for design), as well as that of the ADM1 (recommended for operation/technology development) is shown in Figure 2.

Design: For design, the two most important requirements are that the parameters involved can be identified, and that they represent the key steps in the process. Complicated, structural models are not fully identifiable (Dochain & Vanrolleghem 2001), though partial identification is possible (Batstone et al. 2003). Most papers assessing kinetics have so far been single-step first order models (and also mostly steady state). However, as discussed below, the future critical issues in design of high-rate systems will probably be hydraulics, and sludge behaviour. Therefore, the behaviour of biomass, and substrate particles need to be separated. Therefore, at least a two-stage model (hydrolysis and bioconversion) is required for design purposes. A two-stage model will also allow prediction of organic acids, and mix between soluble/particulate effluent fractions, and is nominally compatible with activated sludge and environmental models. Since complicated model structures greatly increase the computational requirements in complicated hydraulic and particle systems, a minimalist structure should be chosen. In comparison to more complicated models, a simplified two-stage model cannot predict methane composition in the gas phase, or pH without a large number of assumptions. To predict biogas concentration in the liquid stream, it can also be included as an optional state variable.

First order kinetics should be chosen for hydrolysis, for the reasons discussed previously. However, more comprehensive models should perhaps consider the use of Monod kinetics for biological processes. Castillo et al. (1999) found Monod to be unidentifiable compared to first order, but this was a steady state parameter estimation, and dynamics should also be considered. There is some evidence that very low saturation coefficients can exist (Mösche & Jördening 1998), and under dynamic conditions, individual effluent organic acid concentrations may reach above 100 g COD m^{-3} (a commonly recognised K_S). There is no justification for the use of zeroth order models, such as often used for design of high-solids systems.

4.2.1. *Operation/technology development*

Many of the issues with operation and technology development deal with issues related to

specific components (e.g., inhibition, gas transfer, etc). Therefore, to represent these, a complex model is recommended. Because of its transportability, extendibility and wide-spread use, the ADM1 (Batstone et al. 2002) is recommended though the Siegrist model (Siegrist et al. 2002) is also appropriate if butyrate and valerate are not required as outputs.

4.2.2. *Soluble inerts*

Another issue important to both types of models is a non-degradable COD in the influent. An effluent limit of 66 mg l^{-1} was observed by Rodrigues et al. (2003), but it is unknown whether this is dissolved methane or residual COD. However, work on residual COD (soluble microbial products) has indicated similar levels, from digestion of 500 mg l^{-1} skim milk wastewater, with the product characterised as complex organic compounds with varying molecular weight, and with low anaerobic degradability (Barker et al. 2000). This can probably be adequately represented by a single inert state (such as S_I in the ADM1).

4.2.3. *Sulphate reduction*

A major operational consideration is release of odours caused by hydrogen sulphide (H_2S). Sulphates are generally approximately 20 mgS l^{-1} in dilute-moderate domestic wastewater, though levels can be extremely high (50–100 mgS l^{-1}), such that methane production is heavily impacted (Singh & Viraraghavan 1998). For operational and technical development therefore, modelling of sulphate reduction is very important. A extension to the ADM1 has been developed for sulphate reduction (Fedorovich et al. 2003). However, this is complicated, and intended for systems with high sulphate concentrations. A simpler method is to assess sulphate reduction by oxidation of available hydrogen as recommended by (Batstone et al. 2002). An example of this extension is shown in Table 2. It is designed for the ADM1, but can be added to any model that includes hydrogen and bicarbonate as separate states.

This assumes the COD of sulphate (SO_4^{2-}) is zero Additional dynamic states are needed for sulphates (S_{SO_4}), total reduced sulphides (S_{IS}), and sulphate reducers (X_{SO_4}). The kinetic parameters given are set to outcompete hydrogenotrophic methanogens. These are nominal, and should be replaced with properly fitted values. A decay process is also needed (same as all microbial decay processes), with a stoichiometry of −1 for X_{SO_4}. The physiochemical system needs extension to properly describe H_2S/HS^- acid base equilibrium, H_2S stripping, and the impact of the SO_4^{2-}ion on the charge balance. This is described further below. The extension, implemented within the ADM1 is included in Aquasim 2.1d (Reichert 1994) format in supporting material to this paper.

The model was tested with an influent COD of 300 mg l^{-1}, and varying S concentrations (10–100 mgS l^{-1}). It is valid at S:COD ratios of up to approximately 0.1 gS $gCOD^{-1}$, after which the hydrogen is depleted. This equates with maximum of 30 mgS l^{-1} SO_4^{2-} in the influent (300 mgCOD l^{-1}). At higher S:COD ratios, sulphate reducers will start to oxidise organic acids for electrons, and the model of Fedorovich et al. (2003), which describes this, should be used instead. As a basic test, if the simplified model predicts sulphate in the effluent from the reactor, a more complex model is required. A comparison of the simplified model, and that of Fedorovich et al. (2003) is shown in Figure 3.

Above 30 mg l^{-1} influent, sulphide inhibition of aceticlastic methanogens also becomes important, as the free form (H_2S) is inhibitory at levels above 0.002 M {30 mgS l^{-1} as H_2S} (Speece 1996).

4.3. *Kinetic parameters*

Because of correlation between decay rate and uptake rate, it is difficult to separate these two in continuous experiments. Most authors have used a very low decay rate, on the order of 0.01 day^{-1} (see review in Batstone et al. 2002), while the Siegrist model uses decay rates of between 0.05, for aceticlasts and 1, for acidogens at mesophilic conditions (Siegrist et al. 2002), with relatively higher uptake rates (or growth rates). Actually, the outputs from the two parameter sets are directly comparable, with similar results. The uptake rates in the ADM1 need to be increased by 50% to achieve identical results to the Siegrist model. There are now indications that high decay rates are more valid, based on observations from continuous mixed systems (Batstone et al. 2003), and biofilm modelling (Batstone et al. 2004).

Table 2. Sulphate reduction extension for ADM1

Component →	i	8	8a	10	11	12a	23a	Rate (ρ_j, kg COD.m^{-3}.d^{-1})
j	Process ↓	S_{h2}	S_{IS}	S_{IC}	S_{IN}	S_{so4}	X_{so4}	
12a	Sulfate reduction	-1	$(1-Y_{so4})$	$-(Y_{so4})\ C_{bac}$	$-(Y_{so4})\ N_{bac}$	$-(1-Y_{so4})/64$	Y_{so4}	$k_{m,so4}\frac{S_{so4}}{K_{S,so4}+S_{so4}}\frac{S_{h2}}{K_{S,Sh2}+S_{h2}}X_{so4}I_1$
		Hydrogen gas (kgCOD m^{-3})	Sulfides (kgCOD m^{-3})	Inorganic carbon (M)	Inorganic nitrogen (M)	Sulfates (M)	Sulfate reducers (kgCOD m^{-3})	Parameters: $k_{m,so4}$: 50 CODS CODX^{-1} d^{-1} $K_{S,so4}$: 0.0001 M $K_{S,SH}$: 4×10^{-6} kgCOD m^{-3} Y_{so4}: 0.08 CODX CODS^{-1} Inhibition factors: I_1: See Batstone *et al.* (2002)

Hydrolysis parameters for primary sludge are generally between 0.2 and 0.5 day^{-1} at mesophilic conditions (O'Rourke 1968; Eastman and Ferguson 1981; Batstone et al. 2002; Siegrist et al. 2002), and these values are also consistent with apparent hydrolysis rates for particulate COD in wastewater (Castillo et al. 1999). Removal rates of soluble material in the same wastewater were approximately 1.5–2 times faster than particulate material. In comparison, Rodrigues et al. (2003) found much higher rates for the batch phase of an ASBR.

It is very important that proper dynamic experiments be assessed to obtain correct uptake (or growth) and half saturation constants for soluble substrate removal. These can be done either by step or pulse changes in wastewater concentration, or by dilution in the feed to a continuous digester. Some temperature dependency work has been done for overall removal efficiency (Toprak 1995; Zakkour et al. 2001), but this should also be expanded for Monod constants as done by (Siegrist et al. 2002).

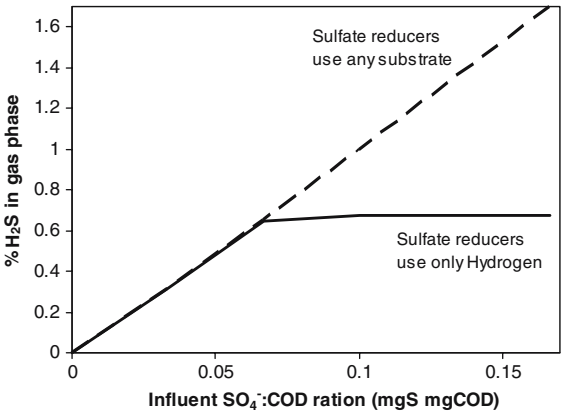

Figure 3. Steady state predictions of % H_2S in the gas phase, against influent S:COD ratio, with proposed model, and model that allows sulphate reducers to oxidise any substrate (Fedorovich et al. 2003). Assumptions are: influent 300 mg COD l^{-1}, no H_2S inhibition, substrate degree of oxidation of $C_n(H_2O)_m$.

4.4. *Physicochemical model*

4.4.1. *Importance of physicochemical components and temperature*

Advanced physicochemical components include prediction of pH, and non-equilibrium gas stripping. pH is not so important in anaerobic sewage treatment, as the ammonia and alkalinity in the wastewater buffers against pH changes to the point of inhibition (Seghezzo et al. 1998). This is also helped by the low influent COD concentrations. However, biogas stripping is very important for predicting methane in the effluent, and product loss. Methane, and gas solubility in general increases with decreasing temperature (Figure 4), and this has an impact on methane release, and inhibition by soluble gases such as hydrogen sulphide and hydrogen. Diffusivity of gases decreases, and viscosity of liquids increase with increasing temperature, which means that the gas–liquid transfer can decrease significantly at lower temperatures. Work at laboratory scale, and mesophilic conditions has indicated strong supersaturation (Pauss et al. 1990), and this should be expanded to full-scale, with varying temperatures. Equilibrium constants can be accurately corrected using the van't Hoff equation as

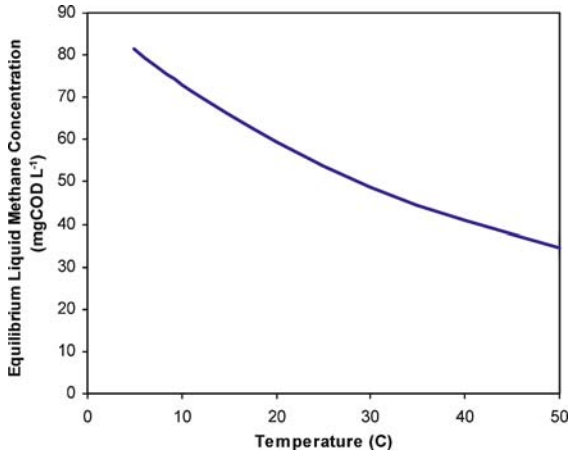

Figure 4. Equilibrium liquid methane concentration versus temperature, based on 0.6 bar methane in gas phase. Temperature correction using van't Hoff equation (Batstone et al. 2002).

in (Batstone et al. 2002), except for acid–base constants for the VFAs.

4.4.2. *Precipitation*

Important precipitants in wastewater treatment include calcium and ferrous/ferric precipitants (mostly with sulphate, sulphide, and carbonate). Struvite is also potentially important for ammonia and phosphorous removal. Precipitation can be modelled relatively readily if the acid–base system is already implemented (Musvoto et al. 2000a; Batstone et al. 2004).

4.4.3. *Sulphide*

In a complex model with sulphate reduction, sulphide acid–base equilibria and hydrogen sulphide stripping should also be included. HS^- and H_2S concentrations should be calculated individually, but S^{2-} should be in low amounts at neutral pH, and need not be calculated unless FeS/Fe_2S_3 precipitation is included. Both acid–base and gas–liquid equilibria follow the van't Hoff equation comparison against measured data from (Speece 1996). Relevant constants are $pK_{a,25C} = 7.05$, $\Delta H^0_{Ka} = 21670$ J; $K_{H,H_2S} = 0.105$ M bar^{-1}, $\Delta H^0_{KH} = -19180$ J (Lide 2001). Implementation is the same as shown in the ADM1 for the bicarbonate/carbondioxide system (Batstone et al. 2002). This physicochemical model is included in the simple sulphate reducing model in the supporting material.

4.5. *Hydraulics*

Hydraulics are a critical element for design, and will probably be a major research topic for effective UASB design in the future. When Monod, or first order kinetics dominate, plug flow reactors are fundamentally more effective than mixed reactors, as higher concentration allows higher removal rates at the start of the reactor. Laboratory reactors have consistently found to be plug-flow (Singal et al. 1998; Batstone et al. 2005), while full-scale industrial reactors are semi mixed (Bolle et al. 1986; Batstone et al. 2005). It is unknown to what extent low-loaded sewage fed UASB reactors are mixed.

Solids handling is a related topic. Granular solids are known to settle within the sludge bed, such that the sludge partitions within reactor height (Bolle et al. 1986; Narnoli & Mehrotra 1997). It is also unknown to what extent substrate particles interact with the biomass sludge bed.

In a review of sewage treatment by UASB reactors, Seghezzo et al. (1998) identified sludge retention, and substrate particle behaviour as the major issue in technology, and modelling as a key method of addressing that issue. I agree, and believe that addressing this aspect, together with hydraulics will allow fundamental improvements in the way low-loaded UASB reactors are designed. Promising work has been done on this issue (Bolle et al. 1986; Narnoli & Mehrotra 1997; Zaiat et al. 2000), but further efforts should be made to co-ordinate and apply this research, especially to low-loaded systems. The biokinetic model underlying the research need not be complex, and the two-stage model shown in Figure 2 contains the major required components of particulate substrate, soluble substrate, particulate biomass, and biogas. Further fundamental analysis of sludge development could include particle population distribution modelling.

4.6. *Modelling for long-term sustainability*

The present review has so far has concentrated mainly on how modelling can improve design and operation of existing and new plants. To achieve long-term sustainability, technology development is required for, especially, the key goals of degassing, and nutrient removal.

Unless a biological solution is found, degassing will mainly involve physicochemical factors that have been already addressed. This can be addressed largely by existing chemical engineering approaches. However, the physicochemical basis of many models can assist in integration of degassing, or biological methane removal within existing systems.

Nutrient removal also has a physicochemical option, through precipitation as struvite and related minerals. This is limited for nitrogen removal, and at higher temperatures. Biological options also exist. Post-aeration is currently used, and can be modelled effectively using the ASM series of models (Henze et al. 1987), which are compatible with the ADM1. Denitrification is limited however, by COD removal in the anaerobic digester. Anammox is a promising technology, which removes ammonia, with nitrite as electron acceptor (Strous et al. 1997). The requirements for organic COD are therefore removed. The nitrate is produced by partial oxidation of a stream containing ammonia. Anammox is starting to be applied to low-concentration wastewaters in UASB reactors (Schmidt et al. 2004). An anammox model compatible with the ADM1 was developed by (Koch et al. 2000), and was applied to the above UASB treating domestic sewage to demonstrate anammox activity.

5. Conclusions

Anaerobic domestic wastewater treatment is developing in importance, mainly in developing countries with a need for low cost, effective wastewater treatment. In particular, UASB technology is likely to be a leader in new installations. Among the main motivations generally used for modelling, the three key motivations for modelling domestic processes is (a) Design: acquisition of design parameters and laws; (b) Operation: optimisation of reactor stability, and prediction of undesirably by-product release (COD, nutrient, and gases); (c) Technology development: develop new technology to further develop long-term sustainability of anaerobic sewage treatment.

Current modelling of domestic sewage projects has concentrated mainly on design, with widespread use of first order models, and steady state solutions. Hydraulics, as well as the behaviour of solids will become important for design, and in order to address this, models will need to be at least two-stage, with hydrolysis and biological steps. Because the hydraulic models will also need to be complex, it is not recommended that a more complicated structural model be used.

Modelling for operational analysis and technology has different requirements. These motivations need a complex model to address. In particular, supersaturation of dissolved gases, production of soluble inert material, and sulphate reduction are key components that are much more important in anaerobic domestic wastewater treatment than in classical anaerobic modelling.

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