

Integrated chemical, physical and biological processes modelling of anaerobic digestion of sewage sludge

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Abstract The biological kinetic processes for anaerobic digestion (AD) are integrated into a two phase subset of a three phase mixed weak acid/base chemistry kinetic model. The approach of characterising sewage sludge into carbohydrates, lipids and proteins, as is done in the International Water Association (IWA) AD model No 1 (ADM1), requires measurements that are not routinely available on sewage sludges. Instead, the sewage sludge is characterised with the COD, carbon, hydrogen, oxygen and nitrogen (CHON) composition and is formulated in mole units, based on conservation of C, N, O, H and COD. The model is calibrated and validated with data from laboratory mesophilic anaerobic digesters operating from 7 to 20 d sludge age and fed a sewage primary and humus sludge mixture. These digesters yielded COD mass balances between 107–109% and N mass balances between 91–99%, and hence the experimental data is accepted as reasonable. The sewage sludge COD is found to be 32–36% unbiodegradable (depending on the kinetic formulation selected for the hydrolysis process) and to have a $C_{3.5}H_7O_2N_{0.196}$ composition. For the selected hydrolysis kinetics of surface mediated reaction (Contois), with a single set of kinetic and stoichiometric constants, for all retention times good correlation is obtained between predicted and measured results for: (i) COD; (ii) free and saline ammonia (FSA); (iii) short chain fatty acids (SCFA); (iv) H_2CO_3 * alkalinity; (v) pH of the effluent stream; (vi) CO_2 ; and (vii) CH_4 gases in the gas stream. The measured composition of primary sludge from two local wastewater treatment plants ranged between $C_{3.38}H_7O_{1.91}N_{0.21}$ and $C_{3.91}H_7O_{2.04}N_{0.16}$. The predicted composition based on mass balances is therefore within 5% of the average measured composition providing persuasive validation of the model.

Keywords Anaerobic digestion; kinetic modelling; sewage sludge; weak acid/base chemistry

Introduction

Recognising the potential usefulness of mathematical models, various researchers have developed such models to describe anaerobic digestion (AD) (e.g. McCarty, 1974; Gujer and Zehnder, 1983; Sam-Soon *et al.*, 1991; Batstone *et al.*, 2002). The early models focussed primarily on the biological processes. Although the importance of the interaction between the biological processes and the weak acid/base chemistry environment in which they operate was recognised early on, because of the effect of pH on the biological processes, modelling this interaction proved as complex as delineating the biological processes. Initially the impact of the biological processes on pH was assessed graphically, based on equilibrium chemistry principles of the carbonate weak acid/base system (e.g. Capri and Marais, 1975).

The advent of computers and development of numerical algorithms made it easier to model the interaction based on single or two phase (aqueous-gas) weak acid/base chemistry equilibrium equations to estimate the pH in anaerobic digesters. The approach of Loewenthal *et al.* (1989) made it possible to include multiple mixed weak acid/base systems, both for estimating the digester pH and in the determination and interpretation of the commonly measured digester control parameters, short chain (volatile) fatty acids (SCFA) and alkalinity (Moosbrugger *et al.*, 1992; Lahav and Loewenthal, 2000).

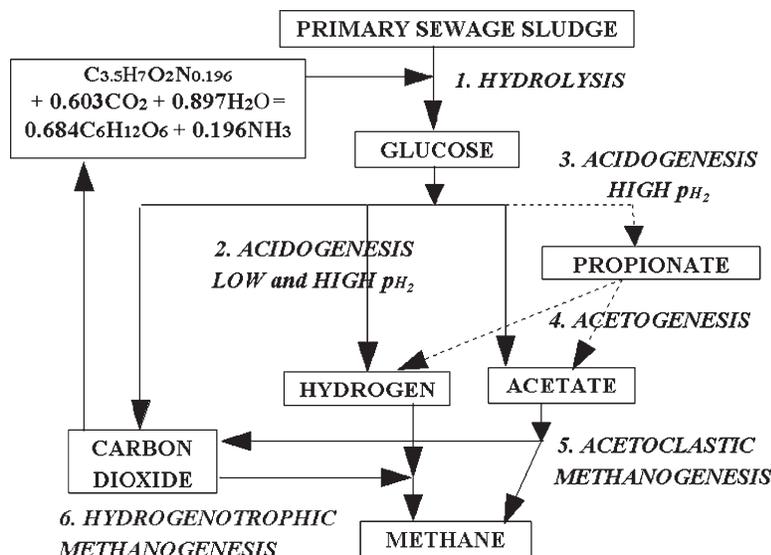
The latest AD model (IWAADM1, Batstone *et al.*, 2002) includes algebraic algorithms, based on equilibrium weak acid/base chemistry and continuity of charge balances, that seek to model the environment in which the biological processes operate, to predict the pH. These algebraic algorithms and calculation of pH operate externally to the kinetic model structure. As an alternative, dynamic equilibria equations for the weak acid/base systems are described (similar to the approach of Musvoto *et al.*, 1997, 2000) but the water weak acid/base system was not included so that pH is again algebraically calculated externally via the charge balance. Calculation of pH externally via the charge balance cannot deal simply with multiple weak acid/base systems in three phases (aqueous/gas/solid), where several minerals competing for the same species may precipitate simultaneously or sequentially (van Rensburg *et al.*, 2003). In some AD systems precipitation of minerals is significant, either within the AD itself or in pipework leading from the AD so that the relevant chemical precipitation processes would require inclusion. For such situations, the biological processes and multiple weak acid/base systems in three phases should be modelled in an integrated way within the same kinetic model structure. This 2-phase (aqueous-gas) AD simulation model is a step toward the 3-phase AD model goal.

Biological processes of anaerobic digestion

Conceptual model

The Gujer and Zehnder (1983) reaction scheme formed the basis for the AD model development, with four main modifications as follows.

- (1) Recognising that carbohydrate, protein and lipid measurements on sewage sludges are unlikely to be routinely available and indeed are difficult to do, the hydrolysis of the three separate organic materials was modified to a single hydrolysis process acting on a generic organic material representing sewage sludge ($C_XH_YO_ZN_A$, McCarty, 1974). This simplification is not unreasonable since the end products of hydrolysis and subsequent acidogenesis of the three organic groups are essentially the same, namely SCFAs. In this approach, the C, H, O and N contents of sewage sludges need to be determined, i.e. the X, Y, Z and A values in $C_XH_YO_ZN_A$. These were determined via COD, C and N mass balances by simulation of measured data and confirmed by direct measurement, see below. In follow-up work to extend the model to AD of waste activated sludges (including biological excess P removal sludges) in three phases (liquid-gas-solid), i.e. including mineral precipitation, the P content of sewage sludges will be added to this formulation (i.e. $C_XH_YO_ZN_AP_B$).
- (2) With the single hydrolysis process, recognition of three separate hydrolysis products was no longer necessary so only a single end product was included. This end product was chosen to be the idealised carbohydrate “glucose” for a number of reasons. The subsequent biological processes on “glucose” are well established and the acidogenic/fermentation process acting on “glucose” to convert it to SCFAs is unlikely ever to be rate limiting. Accordingly, in model application accumulation of “glucose” will not occur, even under digester failure conditions. This implies that the “glucose” acts merely as an intermediate compound, which is acidified to SCFAs as soon as it is produced. In any event, because the end products of hydrolysis and acidogenesis in the scheme of Gujer and Zehnder (1983) are the same as in the revised scheme (Figure 1), the net result is the same in both schemes. In order to maintain the COD, C, H, O and N balances, water and carbon dioxide are taken up from the bulk liquid to generate the glucose from the sewage sludge (Figure 1), and ammonia is released.
- (3) As a consequence of accepting a single hydrolysis process, separate anaerobic oxidation of fatty acids does not need to be included.



S.W. Sötemann et al.

Figure 1 Hydrolysis/acidogenesis cycles

- (4) In the reaction scheme of Gujer and Zehnder (1983), a fixed proportion of hydrolysis end products are converted to intermediate SCFA (propionate, butyrate, etc.) and the balance directly to acetate. As an alternative, the influence of the hydrogen partial pressure (p_{H_2}) on acidogenesis of glucose to acetate and propionate as proposed by Sam-Soon *et al.* (1991) was included in the revised scheme. This provides a better description of AD behaviour under failure conditions. To include the proposals of Sam-Soon *et al.* (1991), the acidogenesis was divided into two processes: (i) under high p_{H_2} conditions, acetic and propionic acids are generated together with H_2 and CO_2 and (ii) under low p_{H_2} conditions, acetic acid only is generated together with H_2 and CO_2 (Figure 1). In this revised scheme, generation of butyrate and higher SCFAs was not considered, because with sewage sludge as influent these usually are only found in minor concentrations, even under digester failure conditions.

Mathematical model – UCTADM1

Accepting the revised reaction scheme (Figure 1), the biological processes mediated by the four recognised AD organism groups were included in the two phase (aqueous-gas) chemical (C), physical (P) and biological (B) anaerobic digestion model (UCTADM1, see Table 1). All four organism groups were accepted to be subject to endogenous respiration and so an endogenous mass loss process was included in the model for each group. In formulating the model, since weak acid/base chemistry is included directly, all biological processes that act on weak acid/base species needed to be formulated in terms of the relevant dissociated or undissociated species. This included both the stoichiometric consumption or production of weak acid/base species by the processes, and the formulation of the kinetic rate expressions. Whichever species is selected, in the production or consumption of weak acid/base species, because the weak acid/base chemistry is included directly, the model will automatically redistribute the weak acid/base species including the hydrogen ion (H^+) and establish a new pH.

The 10 biological processes act on 14 compounds and cause changes in their concentrations, i.e. NH_4^+ , dissolved NH_3 and CO_2 ($H_2CO_3^*$), H^+ (i.e. pH), acetic (HAc) and propionic (HPr) acids, H_2 and CH_4 gases, $C_XH_YO_ZN_A$ (sewage sludge organics), $C_6H_{12}O_6$

Table 1 Biological processes included in the two phase anaerobic digestion model

Process	Specific biological process	Organism group
Hydrolysis Growth	D1. Hydrolysis of $C_xH_yO_zN_A$ to "glucose"	Acidogens, Z_{AD}
	D2. Acidogens on "glucose" under low p_{H_2}	Acidogens, Z_{AD}
	D3. Acidogens on "glucose" under high p_{H_2}	Acidogens, Z_{AD}
	D5. Acetogens on propionic acid	Acetogens, Z_{AC}
	D7. Acetoclastic methanogens on acetic acid	Acetoclastic methanogens, Z_{AM}
Death/Endogenous decay	D9. Hydrogenotrophic methanogens on H_2	Hydrogenotrophic methanogens, Z_{HM}
	D4. Acidogens	Acidogens, Z_{AD}
	D6. Acetogens	Acetogens, Z_{AC}
	D8. Acetoclastic methanogens	Acetoclastic methanogens, Z_{AM}
	D10. Hydrogenotrophic methanogens	Hydrogenotrophic methanogens, Z_{HM}

(glucose intermediate), and the four organism groups Z_{AD} , Z_{AC} , Z_{AM} and Z_{HM} (Table 1). The changes in some compound concentrations may be directly measurable, but the changes in the non-measurable compound concentrations (e.g. H_2 gas) are inferred from the conceptual model of the processes (Figure 1) and mass balance requirements. The compounds and processes of AD based on the reaction scheme of Figure 1 are given in Petersen matrix format by Sötemann *et al.* (2005a). Note that all the compounds are specified as mol/L, including the sewage sludge and biomass. The mol/L of the sewage sludge is calculated from its measured COD concentration and its gCOD/mol, which is calculated from its measured composition, i.e. known X, Y, Z and A in $C_xH_yO_zN_A$ (see below). The AD organism concentrations for all four organism groups are also specified as mol/L based on a formulation of $C_5H_7O_2N$, which has a molar mass of 113 g/mol and a COD/VSS ratio of 1.42 mgCOD/mgVSS (McCarty, 1974). The requirement to express the model compounds in mole units arises from the requirement to model CO_2 production/utilisation (zero COD), which is essential for the weak acid/base chemistry part of the model.

Kinetic modelling of the chemical–physical processes

The reaction scheme for the weak acid/base part of this two phase AD model was taken unchanged from Musvoto *et al.* (1997, 2000). The 16 chemical equilibrium dissociation (CED) processes of the ammonia, carbonate, phosphate, short chain (volatile) fatty acid (SCFA, acetate) and water weak acid/base systems and their 13 associated compounds were included in the AD model. Two additional CED processes had to be added, viz. the reverse and forward dissociation processes for the propionate weak acid/base system, together with its two associated compounds HPr and Pr^- . The 22 chemical ion pairing processes (CIP) with their 13 associated chemical compounds were not included in this two phase AD model, because mineral precipitation (3rd phase) is not yet included.

In the three phase carbonate system weak acid/base model of Musvoto *et al.* (1997), the physical (P) processes for carbon dioxide gas exchange (PGE) with the atmosphere were included, by modelling the expulsion (reverse, K'_{CO_2}) and dissolution (forward, K'_{CO_2}) processes separately and linking the rates for these two processes through the Henry's law constant for CO_2 (K_{HCO_2}), i.e. $K'_{CO_2} = K'_{CO_2} K'_{HCO_2} \cdot RT$. Musvoto *et al.* showed that this approach yielded identical results to the usual interphase gas mass transfer equation with an overall liquid phase mass transfer rate coefficient K_{La,CO_2} , where $K_{La,CO_2} = K'_{CO_2}$. In their model application, the actual CO_2 expulsion rate constant value (K'_{CO_2}) was not important because they considered initial and final steady state conditions only, not the transient dynamic conditions to the final steady state. Also, the CO_2 gas

concentration ($\text{CO}_2(\text{g})$) was kept constant as calculated from a selected partial pressure of CO_2 ($\text{CO}_2(\text{g}) = p_{\text{CO}_2}/RT$), since gain or loss of $\text{CO}_2(\text{g})$ did not need to be determined.

Musvoto *et al.* (2000), van Rensburg *et al.* (2003) and Loewenthal *et al.* (2004) extended this model to include three phase mixed weak acid/base systems to simulate multiple mineral precipitation and active gas exchange of CO_2 and NH_3 during aeration of anaerobic digester liquor and swine wastewater. For CO_2 , they followed the approach of Musvoto *et al.* (1997) above. For the NH_3 , they noted that the atmospheric concentration of NH_3 is negligible (i.e. acts as an infinite sink), so that only NH_3 expulsion need be included, and dissolution could be neglected. Because they simulated transient (dynamic) conditions, the CO_2 gas exchange (as above) and NH_3 gas expulsion (stripping) (and mineral precipitation) rates were important and these were determined from the experimental results. In determining the rates for the gas exchanges, Musvoto *et al.* (2000) noted that, if the dimensionless Henry's law constant of a gas, $H_c [= \{ 1/(K_H R T) \}]$ is > 0.55 , then O_2 can be used as a reference gas and the expulsion rate constant $K'_r (=K_{L,a})$ for the individual gases will be in the same proportion to the rate for O_2 ($K'_{r,\text{O}_2} = K_{L,a,\text{O}_2}$) as their diffusivity is to the diffusivity of O_2 . Of the two gases they considered, only NH_3 has a $H_c < 0.55$ ($=0.011$ at 20°C), so the value for K'_{r,NH_3} had to be determined independently of the values for K'_{r,O_2} , by calibration. For CO_2 , $H_c = 0.95$ at 20°C (Katehis *et al.*, 1998) and accordingly they defined K_{L,a,CO_2} in terms of K_{L,a,O_2} . However, since the compound oxygen was not included in their model, in effect only K_{L,a,CO_2} was determined by calibration against measured data.

In the application here of integrating the biological processes of AD into the two phase (aqueous-gas) mixed weak acid/base chemistry model of Musvoto *et al.* (2000), four gases need to be considered, i.e. CO_2 , CH_4 , H_2 and NH_3 . Of these four, only CO_2 needs to be modelled with both expulsion and dissolution processes, because this gas is significantly soluble. Hence, both dissolved and gaseous CO_2 compounds are included. CH_4 is very insoluble and not utilised in the biological or chemical processes, so its dissolved (aqueous) phase is bypassed and only a gas phase CH_4 compound is included. It is therefore assumed that the acetoclastic and hydrogenotrophic methanogenesis processes (D7 and D9) produce CH_4 gas directly and no CH_4 expulsion and dissolution processes need to be included in the model. Although H_2 is also very insoluble, it is utilised at an interspecies level in the hydrogenotrophic methanogenesis process (D9) and so it cannot be transferred instantaneously to the gas phase. H_2 is therefore modelled as a dissolved compound, but because it is utilised so rapidly and at an inter-organism species level, its residual concentration is extremely small; from a gas production perspective, it can be ignored. Hence, expulsion and dissolution processes for H_2 are not included in the model. NH_3 is readily soluble and its production from organically bound N in the sewage sludge is one of the processes governing the pH in the digester. It can diffuse from the dissolved (aqueous) to the gas phases and so a process for expulsion of NH_3 is included in the model. However, because the rate and quantity of NH_3 expulsion into the gas phase are so slow and low respectively with respect to the total gas production of the digester, in particular in the digester pH range 6.6 to 8, the gas phase is assumed to maintain a negligible NH_3 partial pressure. An NH_3 dissolution process is therefore not included, only an expulsion process (in conformity with Musvoto *et al.*, 2000). Thus, only the $K'_r (=K_{L,a})$ values for CO_2 and NH_3 gases need to be considered. However, because transient conditions are not being modelled in this particular application, but only the final steady state, the expulsion rates of the gases are not important provided the simulation run times are long enough to reach steady state. From the above it is clear that the gas phase partial pressure required in the rate formulations for CO_2 gas exchange need be calculated only from the CO_2 and CH_4 gas concentrations.

Model calibration, verification and validation

The AD model developed above was implemented in the computer programme Aquasim (Reichert, 1998). Details of calibration, verification and validation, which involved setting of kinetic constant values, determination of sewage sludge unbiodegradable COD fraction ($f_{PS'up}$), best hydrolysis rate equation and rate from the Izzett *et al.* (1992) thermophilic AD data set (7 to 20 d retention time completely mixed flow through systems), are given by Sötemann *et al.* (2005a) and are not repeated here. The salient features of this integrated CPB model are discussed below.

Comments on the model

- (1) As an alternative to characterising the sewage sludge feed into carbohydrates, proteins and lipids, as is done in IWA ADM1 (Batstone *et al.*, 2002), it is characterised in terms of total COD, its particulate unbiodegradable COD fraction ($f_{PS'up}$), the short chain fatty acid (SCFA) COD and the CHON content of the particulate organics, i.e. X, Y, Z and A in $C_XH_YO_ZN_A$. This approach characterises the sludge in terms of measurable parameters and allows COD, C and N mass balances to be set up over the anaerobic digestion system. With this approach, the interactions between the biological processes and weak acid/base chemistry could be correctly predicted for stable steady state operation of anaerobic digesters. While not validated for dynamic flow and load conditions, the model has the capability of being applied to such conditions.
- (2) The COD, C and N mass balances and continuity basis of the model fixes quantitatively, via the interrelated chemical, physical and biological processes, the relationship between all the compounds of the system so that for a given biodegradation the digester outputs (i.e. effluent COD, TKN, FSA, SCFA, $H_2CO_3^*$ Alk, pH, gaseous CO_2 and CH_4 production and partial pressures) are governed completely by the input sludge (and aqueous) characteristics. All the kinetic and stoichiometric constants in the model, except those for hydrolysis, were obtained from the literature so that model calibration reduced to determining (i) the unbiodegradable particulate COD fraction of the sewage sludge ($f_{PS'up}$), (ii) the hydrolysis kinetics formulation and associated constants and (iii) the sewage sludge CHON composition, i.e. the X, Y, Z and A values in $C_XH_YO_ZN_A$.
- (3) Interactively with determining the hydrolysis kinetics (see (4) below), the $f_{PS'up}$ was estimated at 0.32–0.36 for primary and humus sludge fed to the mesophilic anaerobic digesters of Izzett *et al.* (1992) ranging over 7–20 d retention time, depending on the type of hydrolysis kinetics selected. These values are very close to 0.36 and 0.33 determined by O'Rourke (1967) and Ristow *et al.* (2004a, b) for “pure” primary sludge and conform closely to that calculated from a mass balance around a primary settling tank with typical raw and settled wastewater characteristics (WRC, 1984).
- (4) Various formulations for the hydrolysis rate of sewage sludge particulate biodegradable organics were evaluated; see below. Surface mediated reaction (Contois) kinetics for slowly biodegradable organics in activated sludge systems were selected. Once calibrated against the Izzett *et al.* (1992) data, this formulation showed the required sensitivity of gas production and unfiltered effluent COD concentration to variation in retention time, without changing the constants in the rate equation.
- (5) From the influent COD, organic N and VSS measurements of Izzett *et al.*, the stoichiometric formulation of the influent sewage sludge was estimated to be $C_{3.4}H_7O_2N_{0.192}$. With the sludge biodegradability and hydrolysis process rate defined, to match the anaerobic digester performance data of Izzett *et al.* (1992) ranging over 7–20 d retention time (i.e. effluent COD, TKN, FSA, SCFA,

H_2CO_3^* Alk, pH, gaseous CO_2 and CH_4 production and partial pressures), the sewage sludge composition was refined to $\text{C}_{3.5}\text{H}_7\text{O}_2\text{N}_{0.196}$ to conform to the COD, C and N mass balances of the model. This formulation was confirmed with primary sludge CHON composition tests, the average of which was $\text{C}_{3.65}\text{H}_7\text{O}_{1.97}\text{N}_{0.19}$. The model predicted CHON content and molar mass of the PS was therefore 95.9, 100, 98.5, 94.5 and 98.7% of the measured values. This provides persuasive validation of the UCTADMI model. A comparison between the model predicted and experimentally measured COD removal, gas production and composition, ammonia and H_2CO_3^* alkalinity generated, and digester pH is given by Sötemann *et al.* (2005b, c).

- (6) With the hydrolysis rate established for the Izzett *et al.* data, simulation of steady state conditions validates only the model stoichiometry because hydrolysis is the rate limiting process under steady state conditions. However, the model, which includes the influence of high hydrogen partial pressure on the acidogenesis and acetogenesis processes, showed the expected sensitivity to a digester upset initiated by temporary inhibition of the acetoclastic methanogens, which is the usual cause in practice. The model demonstrated that even a brief inhibition of this organism group causes an irreversible failure of the digester ($\text{pH} < 6.6$).
- (7) The integrated model demonstrated that the partial pressure of CO_2 and H_2CO_3^* alkalinity generated, and hence the digester pH, is governed almost entirely by the influent sludge composition, i.e. the X, Y, Z and A values in $\text{C}_X\text{H}_Y\text{O}_Z\text{N}_A$, and the influent dissociated SCFA concentration.

The proposed surface mediated reaction (or Contois kinetic) hydrolysis rate equation reproduced the observed change in biodegradable particulate COD acidified versus retention time with the same kinetic constants. Based on the Izzett *et al.* anaerobic digester data, a Monod type hydrolysis rate equation also showed consistency of constants over 7 to 20 d retention time, but simple first order and first order specific hydrolysis rate equations yielded different rate constants at different retention times. However, by changing the unbiodegradable particulate COD fraction of the sewage sludge (f_{PSup}) the fit of both the first order and first order specific hydrolysis rate equations to the experimental data of Izzett *et al.* (1992) could be significantly improved (with concomitant deterioration in the fit with Contois and Monod kinetics). Hence, the Izzett *et al.* anaerobic digester data set is too limited to make a definitive conclusion as to which is the best equation to model the hydrolysis process, and what the best value for f_{PSup} is. Intuitively, and based on its widespread application in activated sludge systems acting on the same biodegradable particulates, the surface mediated reaction (Contois) kinetics has been selected for hydrolysis. Experimental work to *inter alia* refine the modelling of the hydrolysis process is currently being conducted on mesophilic methanogenic and sulphidogenic anaerobic digester systems (Ristow *et al.*, 2004a, b).

The characterisation of sewage sludge in terms of its CHON(P) contents appears a sound approach. While testing primary sludges for the UCTADMI model validation, a range of other sewage sludges were also tested, such as waste activated, anaerobic digested and mixtures of primary and waste activated. From the tests carried out to date, it seems that the CHON contents of sludges are consistent and grouped approximately in conformity with type. It appears likely, therefore, that typical CHON(P) contents of the different sludges may be selected, and that the standard characterisation tests, such as COD, TKN and VSS, are sufficiently discerning and accurate for modelling AD of sewage sludges. Measurement of sewage sludge composition is continuing and its effect on digester pH and gas composition will be evaluated when more information has been collected.

The successful integration in a kinetic way of the two phase mixed weak acid/base chemistry and biological processes of AD has provided a sound basis for further model development. Still to be included in the AD model are mineral precipitation and the P content of sewage sludges. This will extend the model to digestion of biological excess P removal waste activated sludges and provide a direct and quantitative link between feed sludge composition and mineral precipitation problems in digesters.

The integrated physical, chemical and biological processes kinetic modelling approach, applied in this paper to sewage sludge anaerobic digesters and by Sötemann *et al.* (2005d) to biological N removal activated sludge systems, has opened the way to develop a kinetic simulation model for the entire wastewater treatment plant on a materials mass balance and continuity basis. The plant would comprise selected unit operations such as primary settling, biological N and/or P removal from activated sludge and anaerobic or aerobic digestion of waste sludges. With such a model, the impact of wastewater characteristics and type and upstream unit operations performance on downstream unit operations, and the recycling of liquors from downstream unit operations to upstream unit operations, can be assessed for improved and more economical design and operation.

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