A model for anaerobic ponds combining settling and biological processes

K. R. Effebi, H. Jupsin, C. Keffala and J. L. Vasel

ABSTRACT

This work presents an approach to an anaerobic pond model by combining the stoichiometry of the hydrolysis and acidogenic processes of the main constituents of wastewater, i.e. carbohydrates, proteins, and lipids, grouped as a 'combined substrate' with a previously published settling model (see 'Suspended solids settling and half removal time in stabilization ponds (Tunisia)' by Effebi *et al.* (2011)). This approach includes biomass production. Coupling the kinetics and stoichiometry of the previous processes with the usual methanogenic model, we developed an anaerobic pond model. This paper gives the stoichiometry of the different chemical reactions that occur during the degradation of a conventional influent (corresponding to what we define as a 'combined substrate') of domestic wastewater and the model's first results.

Key words | acidogenic, Anaerobic Digestion Model, anaerobic pond, carbohydrate, fat, protein, stoichiometry

K. R. Effebi
H. Jupsin
C. Keffala
J. L. Vasel (corresponding author)
Université de Liège,
Département Sciences et Gestion de l'Environnement,
Unité Assainissement et Environnement,
185 Avenue de Longwy,
6700 Arlon,
Belgium
E-mail: *jlvasel@ulg.ac.be*

K. R. Effebi
University of Abobo,
Adjame,
Abidjan,
Ivory Coast

INTRODUCTION

So far, few non-'black box' models have been developed to describe anaerobic ponds, especially when 'non-steady-state' models are concerned. We have developed a first Anaerobic Digestion Model (ADM)-type anaerobic pond model that combines the settling process and biological processes. The settling efficiency is calculated from a model presented previously (Effebi *et al.* 2011) which will provide the flux of solids flowing from the liquid phase to the sediment compartment. For the biological processes, the main scheme is based on the more general ADM1 (Anaerobic Digestion Model 1) model (Batstone *et al.* 2002). However, the ADM1 model is too sophisticated and would require too many measurements and fitting tests to describe the behaviour of a 'simple' pond. We thus simplified the model by developing the stoichiometry of the hydrolysis and acidogenic processes on the main constituents of wastewater in ADM1, i.e. carbohydrates, proteins, and fats, grouped in a 'combined substrate'. Decreasing the number of state variables and of processes is a well known approach to reduce the complexity of mathematical models. Various authors (Mara 1976; Kamma *et al.* 1994; Morgenroth *et al.* 2002) have provided such compositions for domestic wastewaters. Our approach includes biomass production, combined with activity measurements (Effebi *et al.* 2006), to yield some stoichiometric and kinetic parameters. In this way we consider that we reached the first step of the IWA methodology to develop mathematical models for wastewater treatment processes. A model based on an expert system (knowledge) and the main biological processes yields rather realistic mass balances and the behaviour of the system. Further steps will be to make sensitivity analysis and specific measurements as activities measurements in order to focus on the most important data needed to reach good fitting of the model. In this way we should reach a model that would describe anaerobic ponds properly, and this model is built to be easily combined with similar IWA-type models describing facultative and maturation ponds.

STOICHIOMETRY OF THE MODEL

Starting from a typical main composition of wastewaters (proteins, carbohydrates, and fats), we use the reactions' stoichiometry, including hydrolysis and acidogenic activity and biomass production, to describe a general first step with acetogenesis included and taking into account the corresponding cell yields. In the second step, methanogenesis is

doi: 10.2166/wst.2013.152

described exactly as in the ADM1 model. Figure 1 gives the general scheme of the model's structure.

For example, taking Mara's (1976) wastewater composition:

$$25\%C_6H_{12}O_6 + 65\%C_6H_{14}O_2N_2 + 10\%[CH_3(CH_2)_{14}COOH + C_3H_8O_3]$$
(Glucose) (Protein) (Lipid) (1)

With glucose representing carbohydrates, lysine representing proteins and palmitic acid issued from grease.

The anaerobic degradation of glucose to acetate (including the corresponding yield factor in anaerobic conditions as indicated in Table 1) is taken as:

$$C_6H_{12}O_6 + 0.18NH_3 + 1.16H_2O \rightarrow 0.18C_5H_7NO_2 + 1.7CH_3COOH + 1.7CO_2 + 3.4H_2 \quad (2)$$

For proteins (with lysine as the example and including the corresponding yield factor in anaerobic conditions as indicated in Table 1) the following equation was developed:

$$C_6H_{14}O_2N_2 + 5.44H_2O \rightarrow 0.12C_5H_7NO_2 + 1.8CH_3COOH + 1.8CO_2 + 5.6H_2 + 1.88NH_3 \quad (3)$$

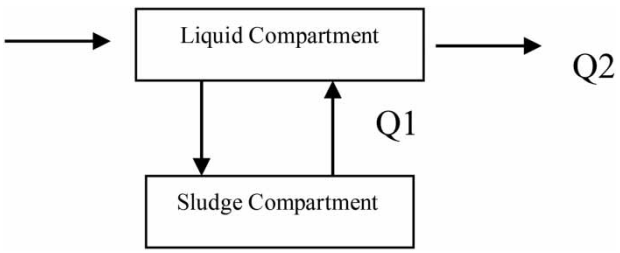

Figure 1 | General scheme of the model's structure.

Table 1 | Anaerobic cell yield coefficients adopted for various substrates (*Y* values selected for the substrates)

	Substrate	Y_{mole} $C_5H_7NO_2$/mol substrate	*Y* COD/COD
IWA (2012)	Glucose	0.18	0.15
	Lysine	0.12	0.51
	Palmitic acid	0.25	0.054
Duncan & David (2001)	Glycerol	0.07	0.1

COD: chemical oxygen demand.

In the case of grease and oils, the degradation process generates glycerol and a long-chain fatty acid (Batstone *et al.* 2002). We took palmitic acid as the prototype. So:

$$C_{51}H_{98}O_6 \text{ (Lipid) yields } CH_2OHCHOHCH_2OH + 3CH_3(CH_2)_{14}COOH$$
Glycerol a long chain of fattyacids (palmitic acid) (4)

Taking into account the corresponding yield factor in anaerobic conditions (Table 1), palmitic acid is subsequently degraded (with biomass production) according to the following equation:

$$CH_3(CH_2)_{14}COOH + 13.26H_2O + 0.25NH_3 \rightarrow 0.25C_5H_7NO_2 + 0.01CO_2 + 7.37CH_3COOH + 14.02H_2 \quad (5)$$

The corresponding equation for glycerol is:

$$C_3H_8O_3 + 0.68H_2O + 0.07NH_3 \rightarrow 0.89CO_2 + 0.88CH_3COOH + 0.07C_5H_7NO_2 + 2.78H_2 \quad (6)$$

Taking the proportions of carbohydrates, proteins, and lipids and yield coefficients (Y) of each substrate in wastewater into account, as indicated above, the following equation is obtained for Mara's proportions:

$$0.139C_6H_{12}O_6 + 0.445C_6H_{14}O_2N_2 + 0.012C_3H_9(CH_2)_{42}C_3O_6H_3 + 0.012C_3H_8O_3 + 3.067H_2O \rightarrow 0.088C_5H_7NO_2 + 1.313CH_3COOH + 1.048CO_2 + 3.502H_2 + 0.801NH_3 \quad (7)$$

Of course, similar equations can be designed for other wastewater compositions as indicated in Table 2.

Thus if we know or if we measure the proportions of carbohydrates, proteins and grease in the target effluent, by combining Equations (2)–(6) with the appropriate proportions (different from Equation (1)), we will reach a final equation similar to Equation (7) containing all the stoichiometric coefficients needed in the model. This can be done easily in a separate Excel® sheet.

Using an equation such as Equation (7), one can define a Petersen–Gujer matrix of the ADM pond model. This equation can be simplified further by grouping all the substrates with their corresponding proportions in a unique

Table 2 | Main constituents of domestic wastewaters. Average is indicated (expressed as a % of total COD) + (standard deviation)

	Proteins (%)		Carbohydrates (%)		Lipids (%)		P + C + L (%)		Others
Authors	Soluble	Total	Soluble	Total	Soluble	Total	Soluble	Total	
Kamma *et al.* (1994)	25 ± 6	28 ± 6	10 ± 7	18 ± 6		31 ± 20		78	22
Henze *et al.* (1982)		8		12		10			70
Tanaka *et al.* (1991)		12		6		19		37	
Mara (1976)		65		25		10			
Metcalf & Eddy, Inc. (1979)				25–50		10			40–60 (organic)

substrate that we will call 'combined substrate'. In the present case we have:

$$C_{4,11}H_{9,08}O_{1,79}N_{0,89} + 3.067H_2O \rightarrow 0.088C_5H_7NO_2 + 1.313CH_3COOH + 1.048CO_2 + 3.502H_2 + 0.801NH_3 \quad (8)$$

(with $C_{4,11}H_{9,08}O_{1,79}N_{0,89}$ as the 'combined' substrate in this case the numerical value of the coefficients are calculated from C,H,O,N mass balances on the left part of Equation (7)). From Equation (8) we can check that total COD values on both sides of the equation are equal as they should be in an anaerobic process and should be checked for each 'combined substrate'. The final Y value is in fact a weighted average of the Y values of the various components and can be calculated for other 'combined substrates'. Biomass production is taken into account, and acetate and H_2 production are also deducted from this equation. This 'complex substrate' biomole (MW = 99.5, COD = 1.55 mg COD/mg) is different from those of Henze *et al.* (1982) ($C_{18}H_{19}NO_9$ with 1.42 mg COD/mg) and also McCarty ($C_{10}H_{19}O_3N$ that is more reduced: 1.99 mg COD/mg); with nitrogen ratios of 0.120, 0.035, and 0.070 mg N/mg, respectively. But it is closer to Sotemann *et al.*'s (2004) biomole of particulate OM in wastewater; $C_7H_{14}O_4N_{0,4}$, yielding 1.57 mg COD/mg and 0.033 mg N/mg. Of course, another biomole will be obtained if we use or measure the composition (carbohydrates, lipids, and proteins) of the target wastewater.

In a further step, acetate and H_2 calculated from Equation (8) are transformed into biogas, and for those steps the usual ADM1 equations, stoichiometry, and kinetics are adopted (Batstone *et al.* 2002).

KINETICS

The kinetic equations of the ADM1 model were kept.

The Petersen–Gujer matrix of the modified ADM1 model is shown in Table 3. It is highly simplified, with seven processes (19 for ADM1) and 11 state variables (24 for ADM1).

Thus the complexity and parameters of the model are drastically reduced by the use of the 'combined substrate' concept, which should help the development of robust models for anaerobic ponds.

A first trial was run to have a preliminary fitting of the model. The data used to facilitate this first step were sludge production, total COD removal efficiency, and activity measurements.

Notice that in the model the decay of biomasses is recycling matter as combined substrate.

ACTIVITY MEASUREMENTS

Activity measurements were performed in the liquid phase and in grab samples collected from the sludge as described by Effebi *et al.* (2006).

As for other biological systems, the activity measurements should be calculated for the corresponding biomasses. But this provides already approximations of the activities. More accurate measurements would be obtained if we combined activity measurements with biomass identification by existing tools from molecular biology.

MODEL STRUCTURE

The hydrodynamics of the model is based on tanks connected in series, where the number of tanks can be obtained from tracer tests (Namèche & Vasel 1996). Moreover, each liquid phase tank exchanges matter as settling occurs in the liquid phase, with the corresponding transfer of solids to the sediment layer (sludge). The settling model is described in more detail in Effebi *et al.* (2011). When the

Table 3 | Gujer–Petersen matrix of the modified model

	State variables	1	2	3	4	5	6	Kinetics (kg CODm^{-3}/d)
j	**Processes**	S_{CS}	$S_{ac.}$	S_{h2}	S_{ch4}	S_{IC}	S_{IN}	ρ_j
1	Hydrolysis of combined substrate	1						$K_{h,CS}{}^{*}X_{CD}$
2	Soluble combined substrate consumption	−1	$(1-Y_{CS})$.A	$(1-Y_{CS})$.B		$-\sum C_i V_{i,2}$ i =1–5,7–11	$N_{cs}-(Y_{CS}).N_{bac}$	$K_{m,ac}{}^{*}(S_{CS}/K_{S,ac}+S_{CS})^{*}$ X_{CD}
3	Acetate consumption		−1		$(1-Y_{ac})$	$-\sum C_i V_{i,3}$ i =1–5,7–11	$-(Y_{ac}).N_{bac}$	$K_{m,ac}{}^{*}(S_{ac}/K_{S,ac}+S_{ac})^{*}$ $X_{ac}{}^{*}I$
4	Hydrogen consumption			−1	$(1-Y_{h2})$	$-\sum C_i V_{i,4}$ i =1–5,7–11	$-(Y_{h2}).N_{bac}$	$K_{m,m}{}^{*}(S_{h2}/K_{S,m}+S_{h2})^{*}$ $X_{h2}{}^{*}I$
5	Combined substrate biomass decay							$K_{deg,CS}.X_{CD}$
6	Acidogenic biomass decay							$K_{deg,ac}.X_{ac}$
7	Hydrogenophilic biomass decay							$K_{deg,h2}.X_{,h2}$
	Balances of reactions $r_i=\sum(V_{ij}).(\rho j)$ j							
	Stoichiometric coefficients A = 0.621, B = 0.412 N_{CS} = 0.801 mole C_{CS} = 1.048 mole Yield coefficient (g COD biomass/g CO substrate) Y_{CS} = 0.091 Y_{ac}, Y_{h2}	Combined substrate (kg COD/m^3)	Total acetic acid (kg COD/m^3)	Hydrogen gas (kg COD/m^3)	Methane gas (kg COD/m^3)	Inorganic carbon (kmolC/m^3)	Inorganic nitrogen (kmolN/m^3)	Kinetic parameters $K_{m,m(ac)}=\mu_{max,m(ac)}/Y_{max,m(ac)}$ K_h, $\mu_{max,ac}$, $\mu_{max,m}$, $K_{S,ac}$ $K_{S,m}$, $K_{deg,ac}$, $K_{deg,m}$, $K_{deg,h2}$ $K_{deg,cs}$, Inhibition

	State variables *i*	7	8	9	10	11	Kinetics (kg CODm^{-3}/d)	
j	**Processes**	X_{cs}	X_{CD}	$X_{ac.}$	X_{h2}	X_I	ρ_j	
1	Hydrolysis of combined substrate	−1					$K_{h,CS}{}^{*}$ X_{CD}	
2	Soluble complex substrate consumption		Y_{CS}				$K_{m,ac}{}^{*}(S_{CS}/K_{S,ac}+S_{CS})^{*}$ X_{CD}	
3	Acetate consumption			Y_{ac}			$K_{m,ac}{}^{*}(S_{ac}/K_{S,ac}+S_{ac})^{*}$ $X_{ac}{}^{*}I$	
4	Hydrogen consumption				Y_{h2}		$K_{m,m}{}^{*}(S_{h2}/K_{S,m}+S_{h2})^{*}$ $X_{h2}{}^{*}I$	
5	Combined substrate biomass decrease (X_{CD})	1	−1				$K_{deg\ CS}.X_{CD}$	
6	Acidogenic biomass decrease (X_{ac})	1		−1			$K_{deg,ac}.X_{ac}$	
7	Hydrogenophilic biomass decrease (X_{h2})	1			−1		$K_{deg,h2}.X_{h2}$	
	Balance of reactions $r_i=\sum(V_{ij}).(\rho_j)$ j							
	Cell yield (g COD biomass/g COD substrate) Y_{CS} = 0.091 Y_{ac} Y_{h2}	Particulate complex substrate kg COD/m^3	Biomass degrading the complex substrate kg COD/m^3	Biomass degrading Hac kg COD/m^3	Biomass using Hydrogen kg COD/m^3	Inert particulate kg COD/m^3	Kinetic parameters $K_{m,m(ac)}=\mu_{max,m(ac)}/Y_{max,m(ac)}$ K_h, $\mu_{max,ac}$, $\mu_{max,m}$, $K_{S,ac}$, $K_{S,m}$ $K_{deg,ac}$, $K_{deg,m}$, $K_{deg,h2}$, $K_{deg,cs}$ Inhibition (I)	

Table 4 | Results of activity measurements compared with the literature

Processes	Substrate	Conc. (g/l)	Activity (g COD/g VSS/d)	References
Acidogenesis (sludge)	Glucose	1.5	0.174	Soto *et al.* (1993)
Methanogenesis (sludge)	Hac	0.125	0.195	Soto *et al.* (1993)
Methanogenesis (sludge)	Hac	0.25	0.394	Soto *et al.* (1993)
Acidogenesis (sludge)	Solubles	–	0.426–0.994	Henze *et al.* (1995)
Methanogenesis (sludge)	Hac	–	0.994–2.13	Henze *et al.* (1995)
Acidogenesis (pure strains)	Glucose	–	13 (max.)	Henze & Harremoes (1983)
Acidogenesis (liquid phase)	Glucose	1.5	0.138	This study
Methanogenesis (liquid phase)	Hac	0.1	0.064	This study
Acidogenesis (sediments)	Glucose	1.5	0.086	This study
Methanogenesis (sediments)	Hac	0.1	0.074	This study

flux of (total) solids from the liquid phase to the sediment compartment is quantified from the settling model, it is converted into a flow rate $Q1$ flowing from the liquid phase, at the solids concentration of the liquid compartment (Figure 1). To maintain mass balances, an equal flow rate $Q1$ is flowing from the sludge compartment (but containing only soluble compounds of the sludge compartment). The above biological processes, described in the Petersen–Gujer matrix can be included in both compartments (liquid and deposits). Table 4 gives the activity measurements in this study compared with the literature.

So far, the process of deposits resuspension, which is most probably related to the biological activities of sediments, is not included in the model.

Table 5 | Main state variables (inlet and outlet) calculated with the model

	Influent	Effluent
Inlet flow rate (m^3/d)	35	35
Soluble fraction (mg COD/l)		
(S_AC)	1	75
(S_CH4)	1	14.§
(S_CS)	225	116
(S_I)	25	25
Total COD soluble fraction	**252**	**230**
Particulate fraction (mg COD/l)		
(X_AC)	1	9
(X_CD)	81	44
(X_CS)	81	61
(X_I)	18	14
Total COD particulate fraction	**181**	**128**

FIRST RESULTS

Based on those assumptions the first results of the model are given in Table 5.

The pond that is being modellized is located in Tunisia. It has been described in more detail in another paper (Keffala *et al.* 2011).

The average values of the measured state variables were used to check the global results of the model. Those results are compared with existing data.

In fact a real steady state will never be reached as some part of the suspended solids (SS) will settle to the sediments. Part of it will be degraded in the deposits and the remaining part will accumulate. The dynamic model is used with estimated initial conditions and is integrated until 'nearly' steady state is reached.

Simulations indicate that with a constant inflow, this 'nearly' steady state is reached within 2 months. From those results the COD balance can be calculated and compared with field data.

The activities (acidogenic and methanogenic), expressed as g COD/g COD/d and thus taking the total of suspended solids as the biomass, which are calculated by the model are still rather different from the measured activities in both the liquid and solid (sediment) phases (Table 6). We can consider that the developed model without any fitting of the parameter so far, yields a rather realistic representation of the system. But the activities calculated from the simulations are still far from the measured activities (Table 7). In the future it will be important to improve the activity measurements and to characterize in greater

Table 6 | (a) COD value (data for inlet and model for outlet). (b) COD values measured at CERTE's (Centre of Water Research and Technologies) wastewater treatment plant (anaerobic pond)

	Inlet	Outlet	Calculated efficiency (%)
(a)			
COD soluble	252	233	7.5
COD particulate	181	129	29
COD total	433	362	16
	Inlet	**Outlet**	**Calculated efficiency (%)**
(b)			
COD soluble	250	220	12
COD particulate	180	150	17
COD total	430	370	14

Remark: % COD soluble: as CH_4 is not very soluble it will be stripped from the water. If we assume that it leaves the water, we reach an efficiency of 13% for soluble COD (Table 6(a)) which is close to the field measurement of 12% (Table 6(b)).

Table 7 | Activities calculated from the model and from field measurements (g COD/g COD/d)

	Kinetic (model)	Measured kinetic
Acidogenesis		
Liquid phase	0.599	0.065
Sediment phase	0.749	0.034
Methanogenesis		
Liquid phase	0.069	0.030
Sediment phase	1.124	0.029

detail the composition of the suspended solids, in such a way that activities would be calculated on the corresponding biomass and not on the total biomass. This would offer an appropriate methodology to fit important kinetic parameters of the model.

Improvements in the model will focus on a better description of the SS concentration in the liquid phase. If we compare our approach to methodologies of models development, as suggested by IWA (2012) on good modelling practice, we can say that we are at the first step of a dynamic model for anaerobic ponds. A rather realistic model is developed taking into account important processes such as settling, acidogenesis and methanogenesis. Sensitivity analysis will help to identify the most important processes in the system in order to focus on methodologies to get the main kinetic parameters of the model. But the model as it is developed will be suitable to be connected with other models describing facultative and maturation ponds, in order to reach a model for a complete system.

CONCLUSIONS

This paper presents a first anaerobic pond model combining the settling process and biological processes. To reduce the model's complexity a 'combined substrate' is defined to combine the hydrocarbon, protein, and lipid contents. The first results are promising, yielding overall COD removal efficiency similar to that measured in the field. We also observed that the anaerobic processes occur not only in the sludge (sediment phase), but in the liquid phase as well.

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First received 8 May 2012; accepted in revised form 7 February 2013