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Abstract
The coupling between a microalgal pond and an anaerobic digester is a promising alternative for sustainable energy production by transforming carbon dioxide into methane using light energy. In this paper, we test the ability of the original ADM1 and a modified version (using Contois kinetics for the hydrolysis steps) to represent microalgae digestion. Simulations were compared to experimental data of an anaerobic digester fed with *Chlorella vulgaris*. The modified ADM1 fits adequately the data for the considered 140 day experiment, and turns out to be a reliable predictive tool.

Keywords
Anaerobic digestion, Chlorella vulgaris, hydrolysis, kinetic model, microalgae

INTRODUCTION

In recent years, microalgae have been widely investigated for biofuel production (Chisti, 2007). Coupling microalgae culture and anaerobic digestion has emerged as a promising process to convert solar energy into methane. Nevertheless, the anaerobic digestion of microalgae faces several hurdles (Sialve *et al*., 2009). A dynamical model of microalgae anaerobic digestion can therefore be of crucial help for apprehending the process complexity and for identifying optimal working strategies.

Modelling of anaerobic digestion has been widely developed since the seventies (Lyberatos and Skiadas, 1999), from simple models (e.g. considering one limiting reaction (Graef and Andrews, 1974) or two reactions (Bernard et al., 2001)) to more realistic representations (e.g. the IWA anaerobic digestion model # 1 - ADM1 - (Batstone et al., 2002) with 19 biochemical reactions). However, to our knowledge, none of these models has yet been applied using microalgae as feedstock. In this paper, we investigate the ability of the Anaerobic Digestion Model 1 (Batstone *et al*., 2002) to describe microalgae digestion. Model simulations are compared with experimental data of anaerobic digestion of the freshwater microalgae *Chlorella vulgaris* (Ras *et al*., 2011).

METHODS

Experimental device

Anaerobic digestion of microalgae was performed over 140 days in a continuously mixed reactor at 35°C without pH control. The reactor was fed by daily additions with a concentrated stock of the freshwater microalgae *Chlorella vulgaris*, harvested after settling. Figure 1 shows the daily dilution rate average together with the substrate additions. For more details on the experiment protocol see Ras *et al*. (2011).

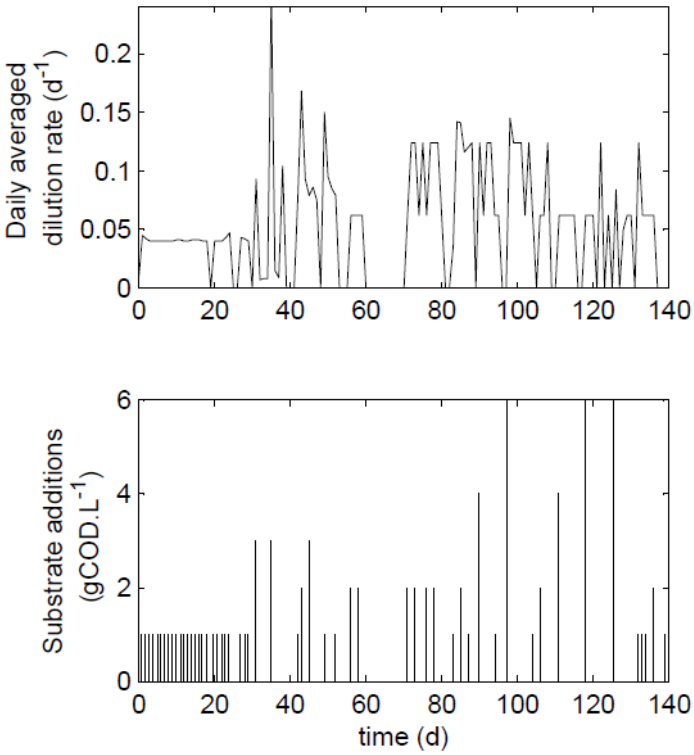

Figure 1. Operating conditions for the anaerobic digestion of the freshwater microalgae *Chlorella vulgaris*.

Modelling approach

ADM1

ADM1 (Batstone et al., 2002) describes the different steps of anaerobic digestion: disintegration, hydrolysis, acidogenesis, acetogenesis, and methanogenesis. This model accounts for 19 biochemical reactions associated to 7 bacterial populations. ADM1 has been widely used to describe the anaerobic digestion of various substrates (Batstone et al., 2006; Parker, 2005).

Modification of the hydrolysis step

Hydrolysis is a complex multi-step process which is not well understood. In ADM1, the hydrolysis rates are taken as first order kinetics. Nevertheless, in some cases, hydrolysis can be better represented by the Contois model (Vavilin *et al.*, 2008), which assumes that the kinetics does not depend on the substrate concentration, but on the amount of substrate per biomass unit. We therefore propose to use the Contois model associated to the benefiting bacteria population. The modifications of the hydrolysis rates are presented in table 1.

Table 1. Hydrolysis rates

Substrate	Rate	Original ADM1	Modified ADM1
Carbohydrate	ρ_2	$= k_{hyd,ch} X_{ch}$	$= k^*_{hyd,ch} \frac{X_{ch}}{K_{S,ch} X_{su} + X_{ch}} X_{su}$
Protein	ρ_3	$= k_{hyd,pr} X_{pr}$	$= k^*_{hyd,pr} \frac{X_{pr}}{K_{S,pr} X_{aa} + X_{pr}} X_{aa}$
Lipid	ρ_4	$= k_{hyd,li} X_{li}$	$= k^*_{hyd,li} \frac{X_{li}}{K_{S,li} X_{fa} + X_{li}} X_{fa}$

ADM1 implementation

ADM1 was simulated using Rosen and Jeppsson (2006) implementation under Matlab. Reaction rates ρ_2, ρ_3, and ρ_4 are taken according to table 1. Moreover, feeding with impulses generates transients in the transfer from the gas to the liquid (i.e. a negative specific mass transfer rate of CO_2 : $\rho_{T,10} < 0$), with pressure in the headspace P_{gas} which can become smaller than P_{atm}. Therefore, the gas flow rate is computed as follows:

$$q_{gas} = max\left(0; k_p(P_{gas} - P_{atm})\frac{P_{gas}}{P_{atm}}\right)$$

where k_p is the pipe resistance coefficient (Batstone et al., 2002).

Influent characterisation

The input characterisation is a critical step in modelling anaerobic digestion (Kleerebezem and Van Loosdrecht, 2006). The inlet concentration was 30 kg COD.m^{-3} with approximately 90% of particulate matter. We assume that the soluble COD is mainly composed of sugars (Hulatt and Thomas, 2010). This leads to $X_{c,in}$ = 27 kg COD.m^{-3} and $S_{su,in}$ = 3 kg COD.m^{-3}. pH in the influent was not monitored but it ranges between 9 and 10 (this high pH results from CO2 uptake by microalgae in the settler). Inorganic carbon in the influent is computed assuming CO2 at equilibrium with its atmospheric partial pressure. Then, pH is computed on the basis of CO2 (= $K_{H,CO2}\, P_{atm,CO2}$), $S_{cat,in}$ and $S_{an,in}$ which drive the charge balance. The input characterisation is given in table 2.

Table 2. Input characterisation (the other state variables are null)

Parameter	Value	Meaning
$S_{su,in}$	3 kg COD.m^{-3}	Sugar concentration
$X_{c,in}$	27 kg COD.m^{-3}	Composite concentration
$S_{IC,in}$	0.019 M	Inorganic carbon concentration
$S_{IN,in}$	0.011 M	Inorganic nitrogen concentration
$S_{cat,in}$	0.024 M	Inert cation concentration
$S_{an,in}$	0.0065 M	Inert anion concentration
pH_{in}	9.6	

Parameter identification

The coefficients $f_{ch;xc}$, $f_{pr;xc}$, $f_{li;xc}$,$f_{xI;xc}$, and $f_{sI;xc}$ represent the fraction of the substrate into the different intermediates, so they have to be identified according to the substrate composition.

The microalgae composition is species dependent but it can also vary with the environmental conditions (Mairet *et al.*, 2011). In non-limited growth, the average biochemical composition (in dry weight (DW)) for *Chlorella vulgaris* is: protein 60%, lipid 20% and sugar 20% (Becker, 2007). Using approximate elemental compositions for protein ($C_{4.43}H_7O_{1.44}N_{1.16}S_{0.019}$), lipid ($C_{40}H_{74}O_5$) and sugar ($C_6H_{12}O_6$) (Geider and Roche, 2002), this biochemical composition leads to a C/N ratio of 5.9, which is in line with the measured ratio of 6. The conversion from g DW to g COD is computed for protein (1.76 g COD/g DW), lipid (2.83 g COD/g DW) and carbohydrate (1.07 g COD/g DW) using the approximate elemental compositions. The inert part is computed from the experimental data of batch experiments (data not shown). Assuming that the inert part composition is equal to the algae's one, we can finally compute the coefficients $f_{ch;xc}$, $f_{pr;xc}$, $f_{li;xc}$,$f_{xI;xc}$, and $f_{sI;xc}$.

Concerning the kinetic parameters, it appears that the pH inhibition terms affect strongly the methanogenesis step while such inhibition was not observed experimentally. Therefore, a lower value of parameter $pH_{LL,ac}$ has been used (5.2 instead of 6). For the original ADM1, the other parameter values were not changed. Parameters of the Contois model are identified by trial and errors to fit the experimental data. Parameter values modified from the original ADM1 are given in table 3.

Table 3. Parameter values modified from ADM1

Parameter	Value	Meaning
Stochiometric parameters		
$f_{sI,xc}$	0	Yield of soluble inert on composites
$f_{xI,xc}$	0.3	Yield of particulate inert on composites
$f_{ch,xc}$	0.08	Yield of carbohydrates on composites
$f_{pr,xc}$	0.40	Yield of proteins on composites
$f_{li,xc}$	0.22	Yield of lipids on composites
N_{xc}	0.0037 kmole/kg COD	Nitrogen content of composites
N_I	0.0037 kmole/kg COD	Nitrogen content of inert
Kinetic parameters		
$pH_{LL,ac}$	5.2	pH inhibition coefficient
$k^*_{hyd,ch}$	3.18 d^{-1}	Maximum specific hydrolysis rate of carbohydrates
$K_{S,ch}$	0.50 kg COD.m^{-3}	Contois half saturation constant of carbohydrate hydrolysis
$k^*_{hyd,pr}$	1.04 d^{-1}	Maximum specific hydrolysis rate of proteins
$K_{S,pr}$	0.26 kg COD.m^{-3}	Contois half saturation constant of protein hydrolysis
$k^*_{hyd,li}$	3.07 d^{-1}	& Maximum specific hydrolysis rate of lipids
$K_{S,li}$	0.49 kg COD.m^{-3}	Contois half saturation constant of lipid hydrolysis

RESULTS AND DISCUSSION

The original version of ADM1 shows a good ability in describing microalgae digestion (see Fig.2 and 3), except at the end of the experiment when a high dilution rate was applied: the model overestimates inorganic nitrogen release. The low experimental ammonium release means that there is an accumulation of nitrogen as proteins X_{pr} or amino-acids S_{aa}. As the soluble COD remains low, we can suppose that there is an accumulation of X_{pr} together with a low protein hydrolysis rate ρ_3. The original ADM1 could not catch these dynamics even after adapting the parameter values.

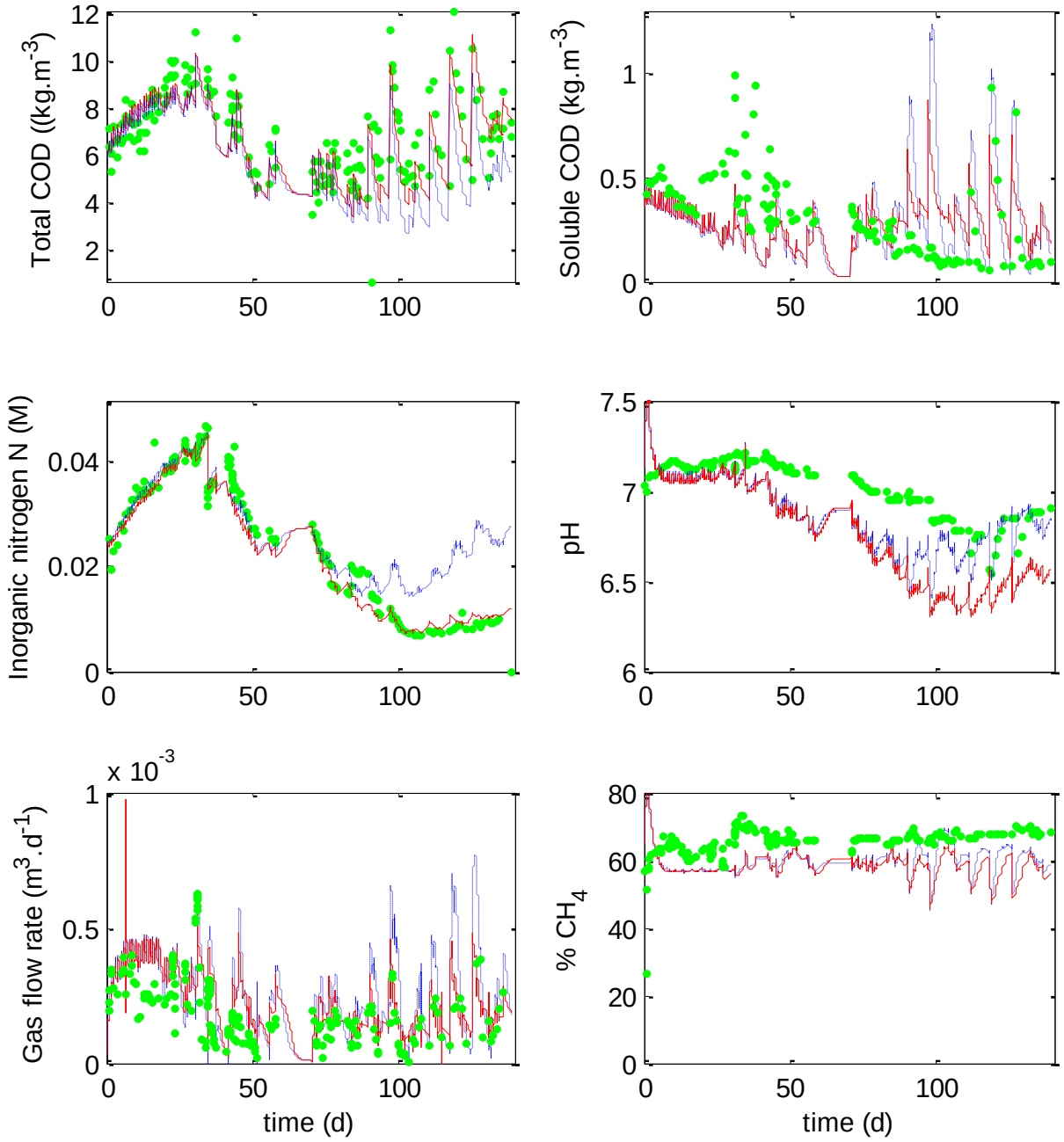

Figure 2. Comparison between the original ADM1 (blue dashed lines), the modified ADM1 (red lines) and experimental data (green dots) of *Chlorella vulgaris* digestion.

The modified ADM1 describes accurately the experimental data. In particular, the good representation of inorganic nitrogen concentrations (Fig.2) is a first hint that including the Contois model for the hydrolysis step in ADM1 improves its ability to describe microalgae digestion.

The model predicts low VFA concentrations (Fig.3), except during transients after the successive increasing inputs at the end of the experiment (after day 100), which is in agreement with the experimental data. The gas flow rate is well predicted (Fig. 2), but the methane content is slightly underestimated. This discrepancy in the methane content is probably due to pH underestimation. A better characterisation of the input should improve the predictions of pH and methane content.

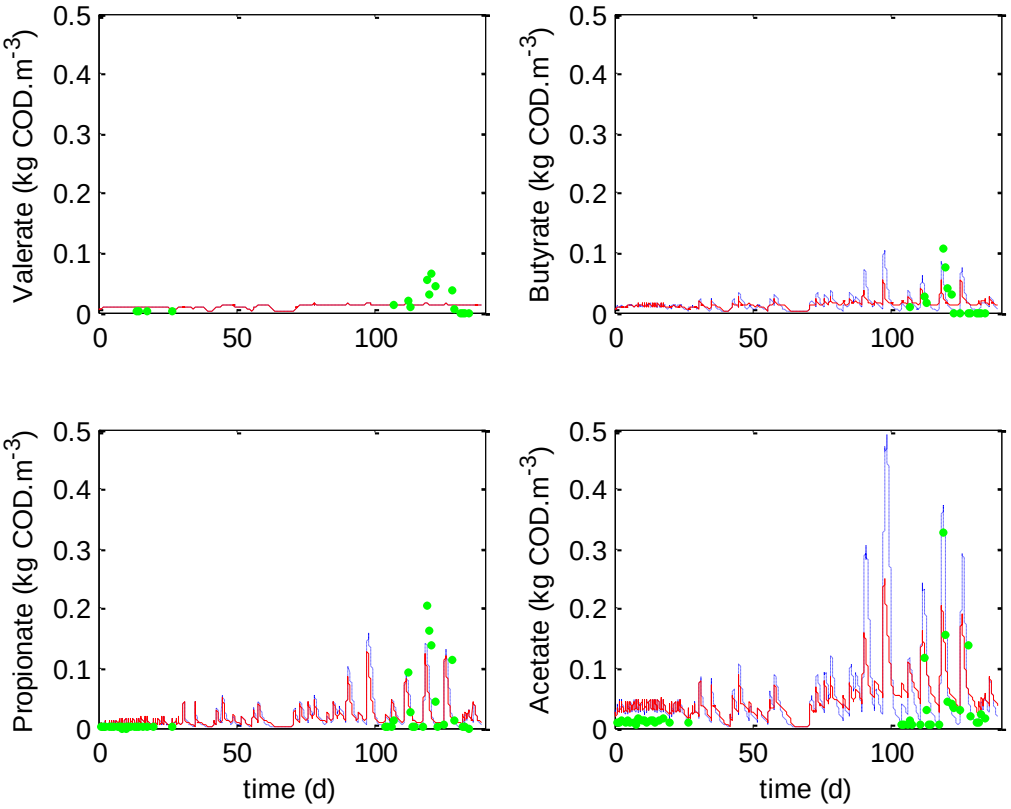

Figure 3. VFA concentrations: comparison between the original ADM1 (blue dashed lines), the modified ADM1 (red lines) and experimental data (green dots) of *Chlorella vulgaris* digestion.

Since all the intermediate substrates or products were not measured separately, estimations of their dynamics can be obtained with model simulation (Fig. 4). From the 50th day onwards, when a high dilution rate was applied, the modified ADM1 predicts an accumulation of protein X_{pr}. On the other hand, carbohydrates and lipids are almost completely hydrolysed because of a higher maximal hydrolysis rates of X_{ch} and X_{li}. This phenomena leads to a release of inorganic nitrogen which was not correlated to the methane production, as it was observed experimentally (Ras et al., 2011).

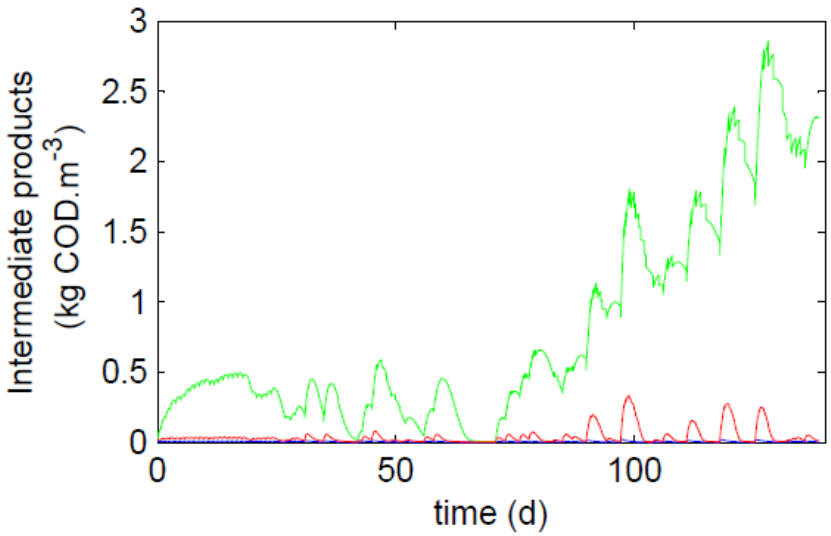

Figure 4. Model prediction of carbohydrate (blue line), protein (green line) and lipid (red line) concentrations during *Chlorella vulgaris* digestion. The high dilution rate at the end of the experiment leads to an accumulation of proteins.

CONCLUSION

In this work, we have proposed a slightly modified version of ADM1 (including Contois model for hydrolysis) for representing anaerobic digestion of microalgae. This model fits adequately the data of the 140 day experiment of *Chlorella vulgaris* digestion.
The ability of ADM1 (originally proposed for activated sludge digestion) to represent microalgae digestion confirms the observation of Ras *et al*. (2011): activated sludge and microalgae digestions show similar trends. Therefore, microalgae digestion could probably benefit of all the improvement obtained with activated sludge (pre-treatment, reactor design, simulation and control...).

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