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ADM1 calibration using BMP tests for modeling the effect of autohydrolysis pretreatment on the performance of continuous sludge digesters

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ABSTRACT

Improving anaerobic digestion of sewage sludge through pretreatment techniques is a suitable solution for better sludge management. In this sense, modeling may present itself as an important tool to assess and predict process performance and pretreatment effects. In this study, the feasibility of using biochemical methane potential (BMP) tests data for calibrating the Anaerobic Digestion Model No. 1 (ADM1) was evaluated, in order to simulate the operation of continuous digesters fed, at different HRTs, with raw and autohydrolysis-pretreated waste activated sludge. This was achieved using a simplified COD fractioning methodology proposed to define ADM1 inputs. Hydrolysis constant rates were determined as the most sensitive parameters, and estimated using BMP tests. The calibrated model was then cross-validated with continuous digesters data sets. Good model performance was attained employing these techniques. The ADM1 was able to successfully represent the consumption of slowly biodegradable organic matter in BMP tests, the changes in hydrolytic limiting steps due to the autohydrolysis pretreatment and the behavior of the continuous digesters in overall. The COD fractioning methodology and the X_c variable manipulation proposed seemed to be crucial for proper model predictions. Results indicate that BMP tests are a suitable data source for ADM1 calibration, and that the model can be a powerful tool to assess the effect of the autohydrolysis pretreatment on the anaerobic digestion of sewage waste activated sludge.

1. Introduction

The adequate treatment and disposal of the surplus of sludge produced by wastewater treatment plants (WWTPs) are an inherent part of any biological treatment layout, requiring efforts in the optimization of systems designed for this purpose. Waste activated sludge (WAS) is one of the main by-products of WWTPs, with increasing importance due to its large production and management costs.

Anaerobic digestion (AD) plays a crucial role in sludge treatment, since it is capable of transforming organic matter into biogas containing 60–70% of methane (CH_4), further reducing the final amount of solids and producing a potential renewable energy source. AD is the most used WAS stabilization technology in Europe (Kelessidis and Stasinakis, 2012) and it is estimated that the annual potential of biogas production in Europe may reach up to 200 billion m^3 (Appels et al., 2008). WAS is mainly composed of microbial cells, which

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possess a membrane that have to be torn down. Therefore, limited biodegradability and slow reaction rates are major limitations of applying AD to its treatment. It is usually accepted that hydrolysis is the rate-limiting step responsible for the aforementioned drawbacks (Li and Noike, 1992; Batstone et al., 2009). For this reason, many pretreatment methods have been studied to improve WAS biodegradability and biogas production, including thermal, mechanical, chemical or biological (Bordeleau and Droste, 2011; Carrère et al., 2010; Pérez-Elvira et al., 2011). Pretreatment enhances the hydrolysis step, making solid substrates more accessible to microorganisms (Fdz-Polanco et al., 2008).

One possible biological pretreatment may be performed by stimulating the microorganisms from the WAS, by subjecting them to different environmental conditions, such as higher temperatures and lower dissolved oxygen concentrations, to produce hydrolytic enzymes (Gavala et al., 2003; Yan et al., 2008). With that perspective, the autohydrolysis pretreatment involves subjecting the secondary sludge to a temperature of 55 °C and a limited amount of oxygen in batch operation, improving the fluidity, ensuring biodegradability and reducing total volume to be treated. In addition, this method can be even more advantageous when the treated sludge contains high concentration of solids and, in fact, the energy requirements for the pretreatment can be covered by the extra energy produced during this process, those requirements being similar to thermophilic digestion and well below thermal hydrolysis (Carvajal et al., 2013).

Modeling is an important tool for assessing aspects of bioprocesses and optimizing biological systems. AD is a complex and non-linear bioprocess, and many different approaches have been used in the last two decades for modeling, parameters identification and validation, with a great variability of results even when the same operational and environmental conditions were applied (Donoso-Bravo et al., 2011). The IWA Anaerobic Digestion Modeling Task Group proposed the Anaerobic Digestion Model No. 1 (ADM1), a structured model that covers multiple steps of the anaerobic digestion (Batstone et al., 2002). The ADM1 includes biochemical steps (disintegration, hydrolysis, acidogenesis, acetogenesis and methanogenesis) and physicochemical processes (ion association/dissociation and gas–liquid transfer). Ever since its development, the ADM1 has been applied to simulate the AD of a wide range of wastes, including sewage WAS (Blumensaat and Keller, 2005), microalgae (Mairet et al., 2011), agro-waste (Galí et al., 2009) and pig slurry (Girault et al., 2011).

Parameter estimation or model calibration is a fundamental procedure in modeling practice before the validation step, which requires a set of experimental data to be performed. Biochemical methane potential (BMP) tests have been widely used to assess the anaerobic biodegradability and the methane production rate for a number of substrates. In the case of hydrolytic-limited processes, BMP tests provide the possibility to estimate the degradation extent (a biodegradability-related parameter) and the first order hydrolysis rate coefficient (Jensen et al., 2011). BMP tests could also be an interesting source of data for calibrating AD models, including the ADM1. In fact, because of their dynamic advantages, batch tests have been employed for parameter estimation in ADM1 modeling studies (Batstone et al., 2004; Girault et al., 2011).

Batstone et al. (2009) employed BMP tests as well as highly variable continuous data for parameter estimation in full-scale systems. The authors reported that BMP parameters were conservative, although the calibrated values were consistent with the average values reported in literature. No information is available, though, whether the same behavior would be observed in other types of system. In this regard, defining the initial conditions for BMP tests represents an important challenge to be overcome, since in batch tests initial conditions are the only inputs of the system. Thereby, the composition of input substrate has a strong impact on anaerobic biodegradability, and is a key factor on determining methane production (Mottet et al., 2010). On the other hand, the ADM1 has a great variety of COD-based inputs, many of them not easily extracted from waste characterization, requiring further investigation.

The aim of this study was to determine the feasibility of using BMP tests as a data source for calibration of the ADM1, in order to evaluate the effects of the autohydrolysis pretreatment on AD of sewage WAS. Initially, sensitivity analyses were performed to select the ADM1 parameters suitable for calibration. The chosen parameters were then estimated using sets of BMP data obtained for (i) raw WAS and (ii) autohydrolysis pretreated WAS. A simplified COD fractioning methodology was proposed to define substrate input in the model. Ultimately, calibrated parameters for both sets of data were employed for cross-validation of the ADM1, using experimental data of two identical continuous digesters fed with raw and pretreated WAS. A model-based assessment of the effects of autohydrolysis pretreatment is also discussed.

2. Material and methods

2.1. Experimental data

2.1.1. Raw and pretreated waste characteristics

Sewage WAS was obtained from the WWTP of Valladolid, Spain, and was concentrated up to 8% of total solids using an industrial centrifugal extractor (Pieralisi, Baby). For the autohydrolysis pretreatment procedure, 500 g of concentrated sludge were loaded in 2 L closed bottles, in such a way that only 25% of the volume was used, and the remaining headspace could contain sufficient air to provide microaerobic conditions. The pretreatment was held for 12 h at 55 ± 0.5 °C with a minimum oxygen concentration of 1.25 mmol O_2 L^{-1} in the headspace. The bottles were continuously agitated by a roller bottle apparatus (Wheaton).

The autohydrolysis pretreatment had a great effect on the solubilization of organic matter, and thus an increase in soluble COD (COD_s) was observed, while total COD (COD_t), total solids (TS) and volatile solids (VS) remained nearly constant. Concentrated WAS characteristics before and after autohydrolysis pretreatment are shown in Table 1.

2.1.2. BMP tests

BMP tests were carried out for raw and pretreated WAS samples in 300 mL flasks, loaded with 150 mL of the corresponding

Table 1 – Raw and autohydrolysis pretreated WAS average characteristics.

	Raw WAS	Pretreated WAS
COD_t (g L^{-1})	83.4 ± 5.7	85.0 ± 4.0
COD_s (g L^{-1})	3.0 ± 0.2	27.0 ± 1.4
TS (g L^{-1})	80.7 ± 4.0	78.0 ± 3.9
VS (g L^{-1})	61.7 ± 5.4	59.0 ± 2.9

concentrated WAS and inoculum at a volatile solids-based substrate/inoculum (S/I) ratio of 0.5 gVS gVS^{-1}. 5 g L^{-1} of sodium bicarbonate were also added as buffer source. Inoculum was obtained from a mesophilic digester treating WAS, and contained 14.2 gVS L^{-1}. At the beginning of the experiment, helium was circulated in the headspace of the flasks. Tests were conducted for 25 days or until no biogas production occurred, in a thermostatic room at 35 ± 1 °C and subject to orbital agitation (150 rpm). Biogas production was measured by a pressure transmitter (IFM, 5 mbar precision) and the methane composition was determined by gas chromatography. Results were plotted as CH_4 volume produced (0 °C, 1 bar) per substrate fed (gVS_{fed}). All the assays were performed in triplicate, and control tests (flasks in which only the inoculum is added) were conducted to discount CH_4 production from the remaining organic matter present in the inoculum. Biodegradability was calculated using the theoretical production of CH_4 based on COD fed (350 mL CH_4 g^{-1} COD) (Mottet et al., 2010).

2.1.3. *Continuous digesters*

Two identical anaerobic digesters (D_1, D_2) were employed and simultaneously operated to treat raw and autohydrolysis pretreated WAS, respectively. They contained 20 L of reaction volume and 10 L of headspace. Both were mixed by sludge recirculation and were operated at 35 °C. Prior to the applying of the actual studying conditions, both digesters were operated for more than 200 days with raw WAS for biomass acclimation purposes. Four hydraulic retention times (HRT) were applied during 220 days of operation, in the following order: 17, 15, 13 and 20 d, corresponding to organic loading rates (OLR) of averagely 3.83, 5.21, 6.08 and 4.24 kgCOD m^{-3} d^{-1}. The mean OLR calculated for the last condition was slightly higher than for the first condition due to an increase in COD concentrations during this last period.

2.1.4. *Analytical methods*

Solids and COD were measured according to the *Standard Methods for the Examination of Water and Wastewater* (2005). COD_s was measured after centrifugation (5000 rpm, 10 min) and filtering (0.45 μm) of the supernatant. Biogas composition was determined by gas chromatography (Varian CP-3800 CG), using helium as carrier gas. Carbohydrate (as glucose) and protein (as casein) contents were measured according to Dubois et al. (1956) and Lowry et al. (1951), respectively.

2.2. *ADM1 implementation*

The ADM1 was implemented in Matlab/Simulink® as a differential and algebraic (DAE) equations system. The implementation followed the guidelines and suggested parameters of Batstone et al. (2002) (with exception of the ones defined by sensitivity analysis and calibrated in this study, as presented below) and the modifications proposed by Rosén and Jeppsson (2006). For application to the BMP tests, the original liquid phase mass balance for a continuous-flow stirred-tank reactor used for validation for D_1 and D_2 was replaced for its corresponding batch form, by removing inlet and outlet flows.

2.3. *Input characterization: COD fractioning*

The ADM1 requires several COD-based inputs in order to define the substrate and inoculum. However, many of the required initial inputs are not easily distinguished based on the available data. For this reason, a simplified COD fractioning criterion is proposed and followed consistently in this study, according to Fig. 1.

For raw WAS, COD_s and particulate COD (COD_p, obtained from COD_t minus COD_s) of the substrate sludge were fractionated in their biodegradable and inert parts, using biodegradability data obtained in BMP tests (50% biodegradable for raw WAS) and considering that this proportion remained the same for both COD_s and COD_p. This was assumed as an approximation, due to the fact that BMP tests do not provide information to specifically determine the biodegradability of soluble and particulate COD separately. Biodegradable COD_s (COD_{sb}) was only divided among sugars, amino acids and LCFA (S_{su}, S_{aa}, S_{fa}), and the other biodegradable soluble inputs were assumed to be zero (S_{va}, S_{bu}, S_{pro}, S_{ac}, S_{h2}, S_{ch4}). Inert COD_s (COD_{si}) was allocated directly to soluble inerts (S_I). Biodegradable COD_p (COD_{pb}) was divided among carbohydrates, proteins and lipids (X_{ch}, X_{pr}, X_{li}) and inert COD_p (COD_{pi}) was divided between particulate inerts (X_I) and composites (X_c), as discussed below. For pretreated WAS, it was assumed that the portion of COD_t that solubilized due to autohydrolysis (COD_{sh}) (Table 1) consisted only of biodegradable compounds. Biodegradable and inert fractions of COD (59% biodegradable for pretreated WAS, according to BMP tests) were thus defined in a similar manner as for raw WAS.

COD proportions between carbohydrates, proteins and lipids (which were extrapolated to sugars, amino acids and LCFA as well) were estimated according to sludge characterization, resulting in 20, 65 and 15% of the corresponding COD, respectively.

As an additional assumption for both raw and pretreated WAS, COD_{pi} was not considered completely non-biodegradable, and 50% of its value was allocated as X_c (which are complex particulates) to account for the reminiscent production of methane even after the 25-day period of the BMP tests. This was done because the calculated biodegradability for BMP tests is related to 25 days of test, and not to complete depletion of biodegradable organic matter. For simulations of continuous digesters this was not applied, since continuous operation did not offer optimum conditions for biodegradation as BMP tests do, and this assumption may lead to an overestimation of the produced methane.

COD measured in the inoculum after the control assays, corresponding to the COD left after biodegradable organic matter contained in the inoculum is consumed, was divided

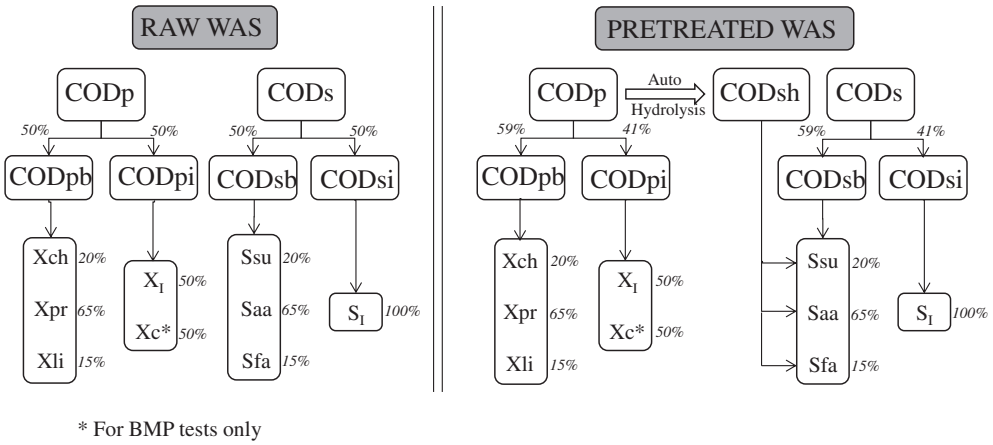

Fig. 1 – Simplified COD fractioning methodology scheme for raw and pretreated WAS. Percentages correspond to COD fractions immediately before each compound.

among the seven biomass inputs of the ADM1 (X_{su}, X_{aa}, X_{fa}, X_{c4}, X_{pro}, X_{ac}, X_{h2}). Since no data was available in regards to the proportion of bacterial groups, division was made in proportion to the corresponding maximum growth rate of each microbial community (μ_{max}), as a rough approximation, for BMP tests. Calibration tests were performed to evaluate the effect of those proportions on the calibrated parameters, and no significant difference was observed when varying systematically the proportions, especially for the parameters corresponding to limiting steps (data not shown). Therefore, this approach did not have an impairing influence on the results. Values used for μ_{max} were the ones suggested by Batstone et al. (2002). For continuous validation, initial biomass conditions were determined according to previous steady-state simulations, as performed by Girault et al. (2012), and described in Section 2.5.

A step-by-step sample calculation for COD fractioning embracing the considerations described above, for both the substrate and the inoculum, is presented in Table 2. The final COD composition of the mixture of substrate and inoculum at the corresponding S/I ratio (0.5) is given in Table 3.

2.4. *Sensitivity analysis*

A sensitivity analysis was carried out to define the most sensitive ADM1 parameters to be calibrated using data from BMP tests. Parameters evaluated were hydrolysis constant rates for disintegration of composites, carbohydrates, proteins and lipids (k_{dis}, k_{hydch}, k_{hydpr} and k_{hydli}, respectively), Monod maximum specific uptake rate (k_m), half-saturation constant (K_S) and yield of biomass on substrate (Y). For k_m, K_S and Y, sensitivity analyses were made for each of the seven different microbial communities. Both biogas production (V_{biogas}) and partial pressure of CH_4 (p_{gas,CH_4}) were set as the focused variables to measure sensitivity in global biogas and methane-

Table 2 – Sample calculation for substrate and inoculum COD fractioning.

	Step	Description	COD value (g L^{-1})
Substrate	1	Define total COD in the substrate	$COD_t = 80$
	2	Define soluble and particulate COD in the substrate	$COD_p = 72$; $COD_s = 8$[a]
	3	Use biodegradability data from BMP tests	$COD_{pb} = 36$; $COD_{pi} = 36$[b] $COD_{sb} = 4$; $COD_{si} = 4$
	4	Use carbohydrates, proteins and lipids characterization data to divide biodegradable COD	$X_{ch} = 7.2$; $X_{pr} = 23.4$; $X_{li} = 5.4$[c] $S_{su} = 0.8$; $S_{aa} = 2.6$; $S_{fa} = 0.6$
	5	Define inerts and allocate 50% of COD_p to composites (X_c) (for calibration with BMP tests only)	For calibration: $X_I = 18$; $X_c = 18$; $S_I = 4$ For continuous validation: XI = 36; $S_I = 4$
Inoculum	1	Define total COD for the inoculum	$COD_{inoculum} = 10$
	2	Define COD left after BMP control assays	$COD_{control} = 6$[d]
	3	Divide $COD_{control}$ between ADM1 microbial populations	$X_{su} = 1.55$; $X_{aa} = 2.07$; $X_{fa} = 0.19$[e] $X_{c4} = 0.63$; $X_{pro} = 0.27$; $X_{ac} = 0.21$; $X_{h2} = 1.08$

a Considering an example in which 10% of the total COD is soluble.
b Assuming a BMP test with 50% biodegradability.
c Considering carbohydrates, proteins and lipids proportions corresponding to 20, 65 ad 15% of the biodegradable COD.
d Considering the control assays consume 40% of the total COD of the inoculum.
e Microbial populations divided proportionally considering each population μ_{max}, listed in the ADM1 guidelines (Batstone et al., 2002).

Table 3 – Proposed COD composition input in the ADM1 to simulate BMP tests.

Soluble (S)	COD_t fraction (%) (raw/pretreated)	Particulate (X)	COD_t fraction (%) (raw/pretreated)
S_{su}	0.21/3.72	X_c	14.50/11.89
S_{aa}	0.71/12.08	X_{ch}	5.80/3.38
S_{fa}	0.16/2.79	X_{pr}	18.85/10.99
S_{va}	0.00/0.00	X_{li}	4.35/2.53
S_{bu}	0.00/0.00	X_{su}	10.34/10.34
S_{pro}	0.00/0.00	X_{aa}	13.72/13.72
S_{ac}	0.00/0.00	X_{fa}	1.25/1.25
S_{h2}	0.00/0.00	X_{c4}	4.13/4.13
S_{ch4}	0.00/0.00	X_{pro}	1.82/1.82
S_I	1.08/0.89	X_{ac}	1.38/1.38
		X_{h2}	7.20/7.20
		X_I	14.50/11.89

specific production. Sensitivity Index (SI) was calculated as described by Jeong et al. (2005), according to Eq. (1).

$$SI = \frac{\sum |C_{STD}(t) - C_{SENS}(t)|}{N} \quad (1)$$

where C_{STD} and C_{SENS} are the simulation results for the standard simulation using default parameters values and the simulation with the new value tested, respectively, for each given time, and N is the number of data. The ranges tested were defined as suggested by Batstone et al. (2002), varying within 30, 100 and 300% depending on the parameter.

2.5. *Model calibration and validation*

The most sensitive parameters were calibrated using data from BMP tests. Therefore, a set of calibrated parameters were obtained for tests with raw and pretreated WAS. For calibration, a least square cost-function measuring the differences between experimental and simulated values was minimized using the fminsearch function from the Matlab® toolset. Cross-validation was performed using continuous operation data from D_1 and D_2 and calibrated parameters for the corresponding type of feeding (raw and pretreated WAS). Substrate concentrations and flow rates were input as temporal vectors to represent the variability of the substrate and HRT along the operation, according to operational data. Before variations on substrate and HRT were input, though, simulations were started with a constant concentration and flow rate for 200 days, similar to those corresponding to the first operational condition. This was performed to assure steady-state conditions both for substrates and microbial populations, which is a good approach to define initial conditions in continuous systems.

3. Results and discussion

3.1. *Parameter sensitivity*

Varying the range of hydrolysis constants, k_m, K_S and Y had different effects on biogas production simulations for BMP

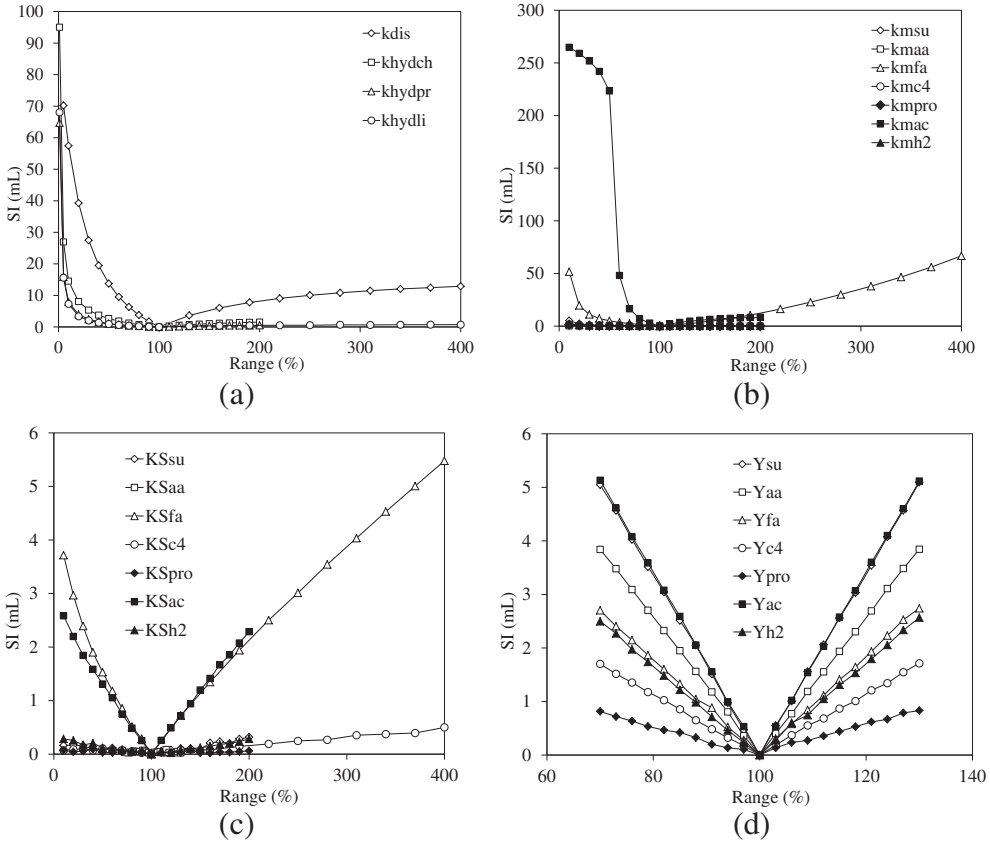

Fig. 2 – Sensitivity indices (SI) calculated for different ranges of (a) hydrolysis constant rates; (b) Monod maximum specific uptake rates; (c) half-saturation constants; and (d) yields of biomass on substrate.

Table 4 – Calibrated ADM1 hydrolysis constant rates for BMP tests performed with raw and pretreated WAS.

	k_{dis} (d^{-1})	k_{hydch} (d^{-1})	k_{hydpr} (d^{-1})	k_{hydli} (d^{-1})	R^2
Raw WAS	0.24	2.38	4.42	1.49	0.9854
Pretreated WAS	5.60	0.72	1.07	3.91	0.9764

tests, as shown in Fig. 2. k_{dis}, k_{hydch}, k_{hydpr} and k_{hydli} all showed asymmetric characteristics and great sensitivity when these parameters were varied at low ranges (Fig. 2a). This is due to the fact that those are the first steps of AD and, at low hydrolysis constant rates, the whole process can be limited by the unavailability of the substrate.

A very strong sensitivity was also observed for k_{mac} at low ranges (Fig. 2b). Low values of k_{mac} caused accumulation of acetic acid, lowering the pH and inhibiting methanogenesis, which resulted in great sensitivity. This result must be dealt with carefully, though, because BMP tests are usually buffered enough to avoid pH drops, and sensitivity in this case would not have great importance. The same is true for k_{mfa}, which showed moderate sensitivity. In this way, even showing considerable sensitivity in Fig. 2b, k_{mac} and k_{mfa} were regarded as less important parameters for calibration, when compared to hydrolysis parameters. K_S and Y presented very low sensitivities (Fig. 2c and d), with SI values below 6 mL. Similar results were obtained setting p_{gas,CH_4} as the focused variable (data not shown). Jeong et al. (2005) also reported that, regarding sensitivity, k_m and Y are not so important, and K_S is negligible.

Based on the sensitivity results, it is reasonable to consider that hydrolysis should be focused for parameter calibration. The sensitivity of all four hydrolysis parameters showed a sharp rise at low ranges, and this is in accordance to the literature regarding the importance of the hydrolysis step in AD (Vavilin et al., 2008; Bordeleau and Droste, 2011). Moreover, the ADM1 suggests as standard parameters a low range k_{dis} (0.5 d^{-1}) and high and equal values of k_{hydch}, k_{hydpr} and k_{hydli} (10 d^{-1}) (Batstone et al., 2002). Such an important part of the AD must be studied more carefully, though, especially when pretreatments affecting the hydrolysis step are involved.

3.2. Estimation of hydrolysis kinetics

ADM1 calibrations resulted in good fits to BMP tests experimental data, with correlation coefficients (R^2) higher than 0.97 (Table 4). Simulation curves showed a crescent behavior all along, following the experimental data tendencies (Fig. 3). Therefore, ADM1 simulations were able to properly represent slowly biodegradable organic matter consumption, with residual increases in CH_4 production at the end of tests.

The limits between inert and slowly biodegradable organic matter seemed to be a very important concept to successfully calibrate the ADM1 using BMP tests data. Considering only biodegradability results at 25 days of test, as described in Section 2.1.2, does not take into account the possibility of some fraction of the organic matter biodegrade after this period. Therefore, allocating a part of what would be initially considered plainly inert (X_I) to the variable X_c was a suitable strategy for better representing the data. Different X_c fractions were tested (data not shown), and allocating 50% of X_I to X_c led to the best calibration results.

Estimated hydrolysis constant rates increased for autohydrolysis pretreated WAS, according to expectations (Table 4). Since hydrolysis in the ADM1 is divided in two steps (disintegration, mainly physical, and hydrolysis of carbohydrates, proteins and lipids, mainly biological), differences were observed as well for the limiting step controlling the global hydrolysis in the ADM1. For raw WAS, the limiting step stayed at disintegration ($k_{dis} = 0.24\ d^{-1}$), and for pretreated WAS, the limiting step moved forward to hydrolysis of carbohydrates ($k_{hydch} = 0.72\ d^{-1}$) and, in a lesser degree, to hydrolysis of proteins ($k_{hydpr} = 1.07\ d^{-1}$). Batstone et al. (2009) and Donoso-Bravo et al. (2010) obtained hydrolysis parameters in the range of 0.15–0.25 d^{-1} in BMP tests, which are close to the limiting step obtained for raw WAS in this study. Similarly, Derbal et al. (2009) reported an estimated value through batch testing of 0.3842 d^{-1} as the lowest of ADM1 hydrolysis constants, when WAS was co-digested with organic waste.

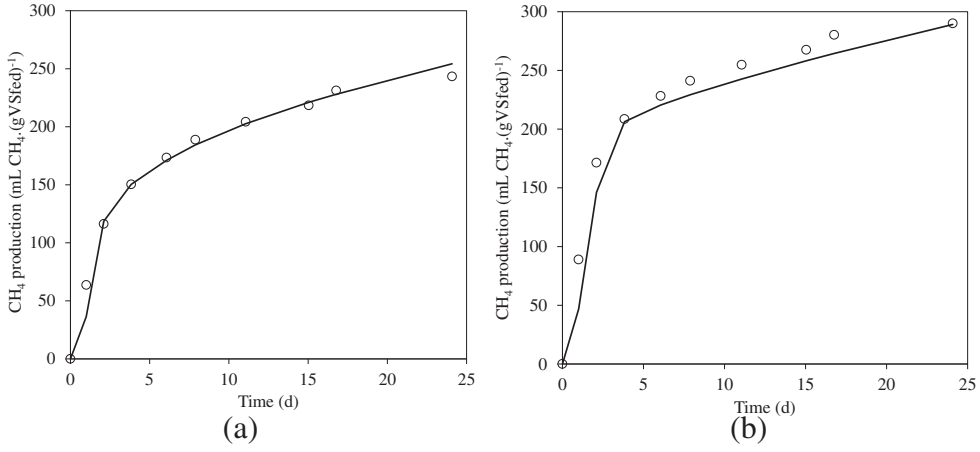

Fig. 3 – BMP tests experimental CH_4 production (○) and ADM1 (–) adjustments with calibrated hydrolysis constant rates for (a) raw WAS and (b) pretreated WAS.

The observed limiting step change is in accordance with what would be expected for autohydrolysis pretreatment. Pretreatment techniques act at the disintegration of the microbial flocs matrix (Appels et al., 2008), making organic matter more bioavailable for the next steps of AD. ADM1 calibrated hydrolysis constant rates seemed to mathematically corroborate this phenomenon, showing that the pretreatment increases the disintegration kinetics of complex organic particles. Non-limiting steps for each case varied more randomly in the calibration, as can be seen in Table 4, probably due to the fact that the minimization procedure suffered a much greater influence from the limiting steps. The other non-limiting constants were mathematically defined in the calibration just as a refining step after the limiting ones were established, causing such variation. Nevertheless, non-limiting steps have little effect in the model outputs when compared to the limiting ones indeed controlling the hydrolysis.

3.3. *Cross-validation*

In general, ADM1 simulations followed reasonably the behavior of the continuous digesters D_1 and D_2. COD_t in the outlet was correctly predicted for both digesters, according to Fig. 4. A similar outlet COD_t curve pattern was obtained for D_1 (Fig. 4a) and D_2 (Fig. 4b), but values for D_2 were lower due to greater consumption of COD_t for pretreated WAS. Simulations for both cases deviated from data at the end of the operation with HRT of 13 d and beginning of operation with HRT of 20 d. When the former was applied, sludge was not adequately concentrated due to operational problems, and feeding characteristics changed, causing a sharp decrease in the inlet COD_t. After such event, experimental COD_t outlet values were not affected significantly, but the model sustained lower values for an increased period, leading to the observed differences.

The model seemed to overestimate CH_4 production at different levels, depending on HRT applied. Blumensaat and Keller (2005) also reported deviations in CH_4 production in response to low HRT and consequent load increases. In the present study, overestimation was more evident at the end of operation with HRT of 15 and 13 d, and in a lesser degree during operation with HRT of 20 d (Fig. 5). In those regions, it was observed that when there was a peak in the experimental CH_4 production and a subsequent drop, the simulated curve followed the event, but sustained higher productions for a longer period than the actual data. The explanation to this may be the fact that inlet COD_t data fed to the model was not as numerous as CH_4 production data (Fig. 4). Therefore, fluctuations in the inlet affected the results produced by the model much more than observed in reality. Another possibility is that, after variations in the inlet like the sharp drop

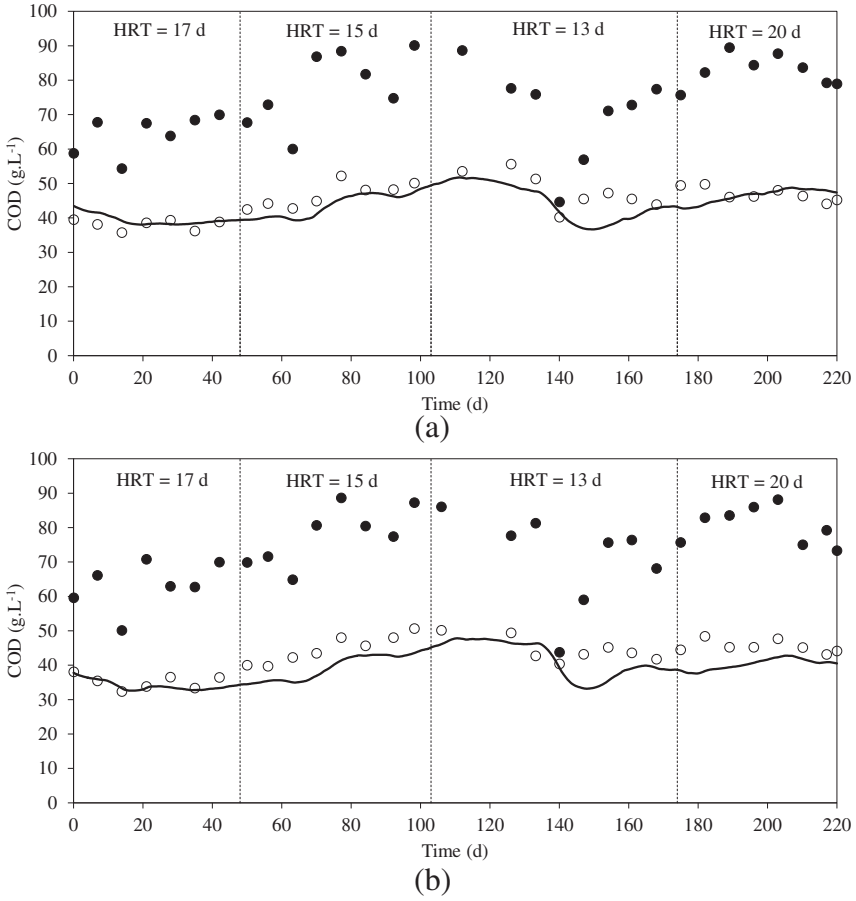

Fig. 4 – COD_t experimental data and ADM1 simulations for D_1 (a) and D_2 (b): (•) experimental inlet, (○) experimental outlet, (–) simulation.

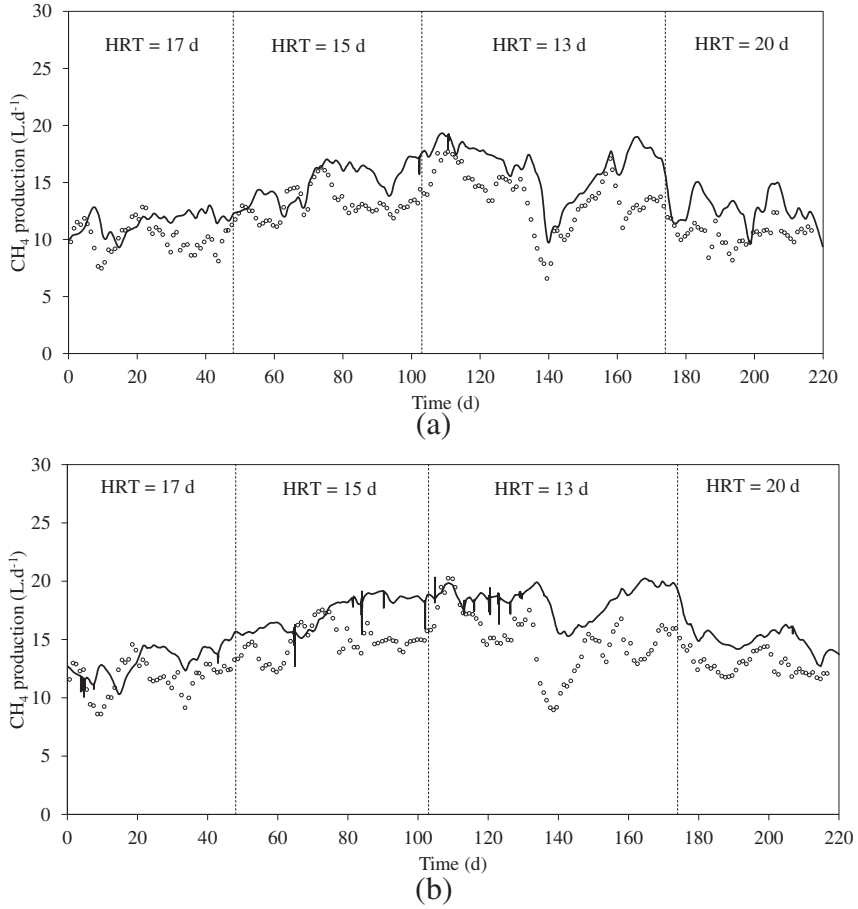

Fig. 5 – CH_4 production experimental data and ADM1 simulations for D_1 (a) and D_2 (b): (○) experimental, (–) simulation.

observed in the operation with HRT of 13 d, digesters could not recover quickly, while the model was more optimistic in this regard.

ADM1 predictions regarding CH_4 production differed in behavior between digesters D_1 and D_2. Predictions for D_1 were more irregular, but followed more closely the peaks and drops of CH_4 production (Fig. 5a), while predictions for D_2 were more smooth, but fluctuating and deviating more from the variation tendencies, as well as presenting some noise due to inconsistencies in pH calculations through algebraic loops (Fig. 5b). Fluctuations for D_2 simulations may be related to the amount of soluble COD present due to the pretreatment, which suffered a great increase when compared to D_1. Nevertheless, model overestimation for methane production was similar to both digesters, according to Table 5, with average overestimation of 17.1 and 17.0%, for D_1 and D_2, respectively, while effluent COD was underpredicted in 3.1 and 8.7%, for the digesters in the same sequence. In overall, it can be assumed that the simplified procedure for COD fractioning and hydrolysis calibration using BMP tests data proposed in this study were adequate to provide enough fit quality and represent the behavior of digesters when changing HRT and varying the inlet characteristics.

Differences between parameter estimation using BMP tests and continuous operation were also observed by Batstone et al. (2009). The authors reported that, when simulating continuous systems, BMP-estimated parameters were too conservative, resulting in poor model performance. In the present study, manipulating the variable X_c was crucial in this sense, since inputting 50% of X_I to X_c was necessary for correct calibration of the ADM1 using BMP tests. However, this procedure was not suitable for simulations for D_1 and D_2, which already overestimated CH_4 production even when no fraction of X_I was allocated to X_c. This may be due to the differences in environmental conditions present in BMP tests and continuous digesters. In the former, optimum conditions are

Table 5 – Overestimation of ADM1 simulations for CH_4 production and effluent COD, when compared to experimental data.

Overestimation (%)		HRT (d)				Average
		17	15	13	20	
CH_4 production	Raw WAS	14.2	14.5	20.2	19.5	17.1
	Pretreated WAS	12.2	16.9	23.4	15.3	17.0
Effluent COD	Raw WAS	4.6	−7.0[a]	−9.0	−0.9	−3.1
	Pretreated WAS	−2.3	−12.7	−8.7	−11.2	−8.7

a Negative values mean underestimation, instead of overestimation.

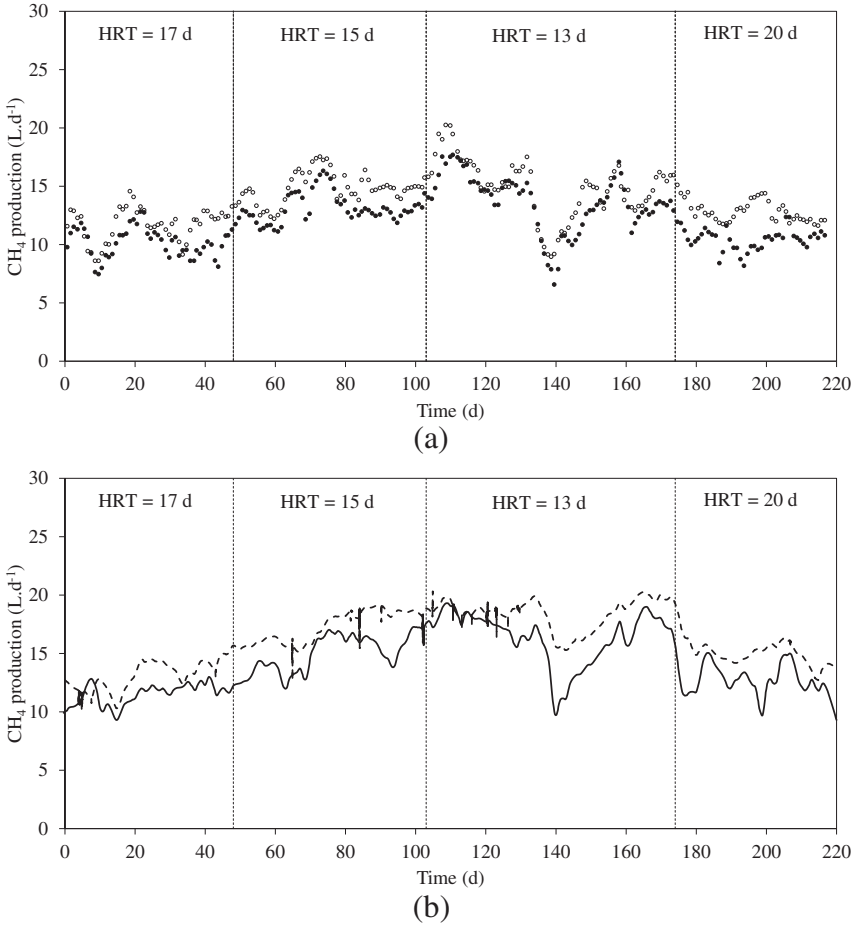

Fig. 6 – Experimental (a) and simulation (b) comparison regarding CH_4 production of D_1 and D_2: (•) experimental D_1, (○) experimental D_2, (–) simulation D_1, (- -) simulation D_2.

maintained, while in the latter conditions are much more critical, and slowly biodegradable organic matter may not be able to degrade at a significant amount for this X_I/X_c strategy to be considered.

3.4. *Autohydrolysis pretreatment effects*

The positive effects of the autohydrolysis pretreatment on CH_4 production are evident in Fig. 6a, showing experimental results from D_1 and D_2. These results corroborate the results generally reported by literature regarding low thermal pretreatment (Wang et al., 1997; Gavala et al., 2003). ADM1 simulations represented reasonably these effects as well, with D_2 simulation containing higher values than D_1 simulation (Fig. 6b). Quantitatively, autohydrolysis promoted the greater effects at the highest HRT (20 d), according to Table 6. Operation with a higher HRT probably took more advantage of the disintegration of complex organic compounds than lower HRT, although this is not expected and may be related to high concentrations of solids in the feed and operational variability. From a modeling perspective, though, the model seemed to predict that as well, because simulated CH_4 production increments were close to the experimental ones (Table 6). Therefore, the assumptions made in this study and considerations regarding organic matter solubilization in the COD fractioning methodology were enough for predicting the effects of the autohydrolysis pretreatment successfully. These results indicate that the ADM1 model can indeed be a powerful tool for predicting improvements in digester performance when pretreatment is applied.

Table 6 – Autohydrolysis pretreatment effect on the increasing of CH_4 production for experimental data and simulated results.

	HRT (d)			
	17	15	13	20
Experimental (%)	15.9	13.5	10.0	23.9
Simulated (%)	13.2	15.6	12.5	19.0
Overprediction (%)	−17.0[a]	15.6	25.0	−20.5

a Negative values mean underestimation, instead of overestimation.

4. Conclusions

Using BMP tests was a suitable choice for calibrating ADM1 hydrolysis parameters. The model was able to correctly

represent the consumption of slowly biodegradable organic matter in such tests, define changes in the hydrolytic limiting step caused by the autohydrolysis pretreatment and predict continuous digesters behavior at different HRT conditions with good accuracy. The simplified COD fractioning methodology used in this study, as well as the adequate X_c manipulation, were crucial factors for good model prediction, showing the importance of those subjects for proper modeling of AD. In overall, the ADM1 model proved to be a powerful tool to assess the effects of the autohydrolysis pretreatment on the AD of sewage WAS.

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