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Modelling of anaerobic treatment of evaporator condensate (EC) from a sulphite pulp mill using the IWA anaerobic digestion model no. 1 (ADM1)

F. Silva [a], H. Nadais [a], A. Prates [b], L. Arroja [a], I. Capela [a,*]

[a] CESAM, Environment and Planning Department, University of Aveiro, Portugal, Campus Universitário Santiago, 3810-193 Aveiro, Portugal
[b] Caima – Indústria de Celulose S.A., Constância Sul, 2250-058 Constância, Portugal

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ABSTRACT

This paper presents the application of the ADM1 model to simulate the dynamic behaviour of an anaerobic reactor treating the condensate effluent (EC) generated in a sulphite pulp mill. The model was implemented in the simulation software AQUASIM® 2.1d and its predictions were compared to experimental data obtained in lab-scale semi-continuous assays treating the industrial effluent. Sensitivity analysis revealed high influence of kinetic parameters on the process behaviour, which were further estimated: maximum specific uptake rate ($k_m = 13.2\ d^{-1}$) and half-saturation constant ($K_s = 0.06\ kg\ COD\ m^{-3}$). The accuracy of the optimised parameters was assessed against experimental data from a second lab-scale reactor treating EC effluent with an additional carbon source (molasses). It was concluded that the model predicted reasonably the dynamic behaviour of the anaerobic reactor under different loading rates. In addition, simulations successfully predicted a better stability and performance of the process (lower VFA accumulation and higher COD removal and methane production) for the EC treatment when an external carbon source is added to the reactor, specifically at high organic loads (2 kg COD m^{-3} d^{-1} or higher). The model was not able to describe adequately the reactor behaviour at high organic loads when molasses was not added, thus application of the model for the anaerobic treatment of EC effluent needs to be further evaluated.

1. Introduction

Sulphite pulping is one of the chemical pulping methods used in pulp and paper industry. In this process sulphurous acid and sulphite are added into the wood digester to extract the cellulose from the wood chips. The cooking liquor is condensed in the evaporator system to reuse the chemicals [1]. The resulting liquid current (evaporator condensate, EC) is a stream that contains acetic acid, which makes it suitable to be pre-treated by anaerobic digestion, before joining the other process streams in an activated sludge process. The potential advantage of this procedure is that this waste stream is warm and contains low molecular weight organic compounds that are readily metabolised to methane by anaerobic bacteria [2]. In spite of a general good running of this anaerobic treatment process, the substrate by itself may occasionally cause inhibition and stability problems in the digester [3]. Additionally the wastewater from chemical pulping processes contains a large fraction of recalcitrant materials which are generally toxic to bacteria, requiring adaptation of anaerobic sludge [4]. In this sense, there is certainly a need to find a way to keep a good performance and to improve stability of this particular wastewater treatment process.

Having EC a significant acetic acid content, the anaerobic consortium that metabolises this substrate becomes predominant, which means poor biodiversity and dominance of methanogenic bacteria inside the reactor treating this current. It is widely reported that, above all the anaerobic community, the methanogenics are those with slower growth and lower kinetic rates, and so a longer time is required to adjust to organic and toxic shock scenarios. The use of an external carbon source, such as sugarcane molasses, will promote the development of other types of microorganisms, mainly acidogenics and acetogenics, which may improve the stability and

Abbreviations: COD, chemical oxygen demand (kg COD m^{-3}); EC, evaporator condensate; kdec_xac, decay rate for aceticlastics (d^{-1}); k_m, maximum specific uptake rate for lumped substrate (d^{-1}); km_ac, maximum specific acetate uptake rate (d^{-1}); K_s, half-saturation constant for lumped substrate uptake (kg COD m^{-3}); Ks_ac, half-saturation constant for acetate uptake (kg COD m^{-3}); M, molasses; OLR, organic loading rate (kg COD m^{-3} d^{-1}); S_{ac}, soluble acetate (kg COD m^{-3}); S_{ac_ion}, soluble acetate (ionised form) (kg COD m^{-3}); SC 1, semi-continuous assay without molasses addition; SC 2, semi-continuous assay with molasses at CL:M = (40:1) COD ratio; S_{CH4_gas}, methane in gas phase (mol L^{-1}); sCOD, soluble chemical oxygen demand (kg COD m^{-3}); S_{H+}, hydrogen in liquid phase (mol L^{-1}); S_{su}, soluble sugars (kg COD m^{-3}); VFA, volatile fatty acids (kg COD m^{-3}); VSS, volatile suspended solids (kg COD m^{-3}); Y_ac, yield of biomass on acetate (dimensionless).

* Corresponding author. Tel.: +351 234370200x22604; fax: +351 234270309.
E-mail address: icapela@ua.pt (I. Capela).

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performance of the overall process. Molasses is a by-product of the sugar refinery process and it contains a high sugar content ranging from 48 to 50%, mainly sucrose, glucose and fructose, a water content of 17–25% and polysaccharides (dextrin, pentosans, polyuronic acids) containing of 2–5%. Its reduced polymeric sugars can further react to form fermentable sugar during enzymatic hydrolysis [5,6]. Many researchers have mentioned molasses as a cheap external carbon source for several biotechnology applications, such as ethanol and citric acid fermentation [6], alcohol and amino acid production, baker's yeast fermentation, improvement of biological denitrification, or biological sulphate removal.

Modelling techniques may be used to predict process behaviour at different scenarios and to assist operational management to develop strategies to improve stability. Several mathematical models are often developed for wastewater engineering applications as an excellent method of conceptualising knowledge about a process and to convey it to other people. Models are also useful for formulating and testing hypothesis and for incorporating new ideas that can later be verified or discarded in reality [7]. The modelling efforts can also be a valuable tool for predicting the performance of full-scale treatment operations, either in steady-state, or in changeable load conditions. On the other hand, the application of sophisticated methods for process control is only possible if mathematical models are available for the system to be optimised [8].

Recently a high-level model, known as anaerobic digestion model no. 1 (ADM1), was achieved with an agreement between many experts in anaerobic digestion and dynamic modelling. This model describes complex substrates by their complete organic and inorganic composition and consists of several steps to simulate all possible reactions occurring in anaerobic biodegradation including not only biological reactions but also physico-chemical processes such as ion equilibria and liquid–gas transfer. Hence, ADM1 aimed at the creation of a common platform from which simulations for a wide range of specific processes should be developed. In fact, the scientific research has been encouraged to contribute specific model modifications, widening and validation studies [9]. Several researchers have implemented this tool and proved its success in simulating a wide spectrum of anaerobic treatment applications such as: municipal wastewater sludge [10] and recycled-paper mill wastewater [11].

The purpose of the present study consisted on the application of the ADM1 model to simulate the dynamic behaviour of an anaerobic reactor treating a specific current from a sulphite pulp mill (EC effluent). Additionally, another aim was to predict and optimise the process for high loading rates, using an external carbon source to increase process stability. The model was calibrated using lab-scale data from a semi-continuous reactor treating EC effluent and, for validation purpose, data sets from a second lab-scale reactor treating the EC effluent with a small molasses addition were used. To date, little or no experience exists in EC treatment modelling. This study aims to contribute with further information on the use of ADM1 model for simulations, as well as to outline good procedures related to the operation of a full-scale anaerobic reactor treating EC effluent at high organic loading rates (OLR) without time-consuming and expensive experimental measurements.

2. Materials and methods

2.1. Experimental set-up

Semi-continuous assays were performed in order to provide some data for parameter estimation and model validation. Two parallel assays were conducted using continuously stirred 5 L glass contact reactors, properly maintained under anaerobic and mesophilic environment (35 °C).

Table 1
Experimental matrix of the SC1 assay (without molasses)

Organic loading rate ($kg\,COD\,m^{-3}\,d^{-1}$)	Run time (d)	Flow rate ($10^{-6}\,m^3\,d^{-1}$)	Fed EC ($kg\,COD\,m^{-3}$)
0.09	0–5	200	2.347
0.14	6–10	200	3.547
0.20	11–15	200	5.043
0.30	16–20	200	7.542
0.43	21–26	200	10.693
0.55	27–30	240	11.500
0.87	31–35	350	12.483
1.22	36–40	550	11.093
1.69	41–45	750	11.267
2.31	46–50	1000	11.556
2.61	51–55	1150	11.352

The reactors were inoculated with anaerobic sludge from a full-scale reactor treating EC effluent, corresponding to a concentration of 7 g VSS L^{-1}. Each day a volume of mixed liquor (defined in Tables 1 and 2 as flow rate) was removed and taken as sample, and then an equal volume of feed was added in a manner to prevent introduction of air in the system. For reactor SC1, the feed consisted of EC previously neutralised with NaOH, as well as distilled water, inorganic nutrients and sufficient alkalinity as $CaCO_3$ to ensure a neutral medium and providing the system with some buffer capacity. For the SC2 reactor, the feed consisted of all constituents of reactor SC1 plus a molasses addition at the proportion EC:M = 40:1 in a COD basis.

In Tables 1 and 2, each of the defined organic loading rates (OLR) was tested for a period of 4–5 days and was monitored by daily routine analysis of soluble chemical oxygen demand (sCOD), methane production, pH and volatile fatty acids (VFA).

All the analyses were performed in accordance with standard analytical procedures [12]. Alkalinity and pH were measured with "Mitsubishi GT-Automatic Titrator" (methods 2320B and 4500-H^+ B). COD was measured by colorimetric method using "Aqualytic COD vario PC compact" equipment (method 5220D). The solids analyses were performed with glass microfibre filters "GF3" (47 mm diameter), analytical balance "Precisa XB120", drying oven "Shimadan" and muffle furnace "Termolab SR-24" (methods 2540B, 2540D and 2540E).

Produced biogas was measured by water displacement and the gas content analysis was done by collecting a sample with a syringe and submitting it to gas chromatography on "SRI 8610C" equipment with TCD detector. The VFA were also analysed by gas chromatography on "Chrompack CP 9001" equipment with FID detector.

2.2. Model description and implementation

The ADM1 is described in the scientific and technical report prepared by an IWA Task Group [9]. This model takes into account seven bacterial groups as particulate matter suitable for modelling. The biological degradation pathways are described using Monod kinetics. The extracellular steps (disintegration and hydrolysis) and the biomass decay processes are described using first-order

Table 2
Experimental matrix of the SC2 assay (molasses addition of 2.5% COD basis)

Organic loading rate ($kg\,COD\,m^{-3}\,d^{-1}$)	Run time (d)	Flow rate ($10^{-6}\,m^3\,d^{-1}$)	Fed EC ($kg\,COD\,m^{-3}$)	Fed molasses ($kg\,COD\,m^{-3}$)
0.14	0–4	200	3.460	0.086
0.29	5–8	200	7.063	0.177
0.84	9–12	200	20.553	0.514
0.94	13–16	200	22.829	0.570
2.08	17–20	350	29.008	0.725
2.49	21–25	360	33.743	0.844

Table 3
Characterisation of the currents under study and the anaerobic biomass (average ± standard deviation)

Parameter	Evaporator condensate (EC)	Molasses (M)	Anaerobic biomass
COD ($g\,L^{-1}$)	13.8 ± 0.9	1087 ± 20.3	194 ± 15.5
Total VFA ($g\,COD\,L^{-1}$)	3.56 ± 0.05	295 ± 1.5	na[a]
Acetate (S_{ac}) ($g\,COD\,L^{-1}$)	3.18 ± 0.04	131 ± 0.5	na[a]
pH	2.4	6.8	7.4
SO_2 ($g\,L^{-1}$)	0.39 ± 0.04	na[a]	na[a]

[a] Not available.

kinetics. As proposed in the original model concept, it is assumed that there is no biomass accumulation and hence, the hydraulic retention time equals the solids retention time [13].

For reactors simulation, ADM1 was implemented with the software AQUASIM® 2.1d, which also provides sensitivity analysis and parameter estimation tools. Ammonia forms (NH_3 and NH_4^+), hydroxide and hydrogen ions (OH^- and H^+) and volatile acids ionic forms were implemented as algebraic variables, while inorganic carbon components (CO_2 and HCO_3^-) were implemented as dynamic states as proposed by Rosen and Jeppsson [14]. Initially all the parameters were set by the recommended values of ADM1 without modifications [9]. After an extensive period of consistency checks in steady state conditions, the experimental SC1 scenario was simulated for verification and parameter estimation, and then validation was performed using the SC2 scenario.

2.3. Model inputs and initial conditions

The main characteristics of evaporator condensate (EC) and molasses (M) are shown in Table 3. The input conditions were based in this characterisation and in the experimental loading rates presented in Tables 1 and 2. Considering that lumping substrates can simplify the model for complex substrates making it easier to implement and apply, as well as it also allows a better parameter identifiability [15], it was assumed that all COD fed to SC1 reactor is converted to soluble acetate (S_{ac}). Moreover, acetic acid accounts for the majority of the volatile acidity present in EC. Other components present in the effluent are then integrated as a lumped substrate to model, as they are assumed to be convertible to soluble acetate. Despite this lumping methodology leads to consider virtually soluble acetate as the main substrate initially present inside the reactor, model fitting will give estimations for EC degradation parameters. The components not assumed for reactor simulation were set as inert components (S_I) at model input, equally varying in steps accordingly with the EC influent concentration increase.

For the SC2 scenario, a feeding of 2.5% of soluble sugar (S_{su}) and 97.5% of soluble acetate (S_{ac}) was assumed. For both reactors it was also assumed a small fraction of inorganic carbon entering the system which was progressively increased with the loading rate increase (varying from 0.03 to 0.3 $mol\,L^{-1}$), accordingly with the need for increasing the neutralising agent addition. Concentrations of metallic cations (namely Na^+) were also included in the input. The main characteristics of the components inside the reactors (EC effluent, molasses and anaerobic biomass) were set up as input concentrations or initial values.

The initial conditions applied to major variables of the implemented model are described in Table 4. With the exception of the biomass variables, all the initial conditions were based in model outputs at steady state under the lowest OLR applied (0.10 $kg\,COD\,m^{-3}\,d^{-1}$). The experimental set-up initially contained a biomass concentration of 7 $g\,VSS\,L^{-1}$ inside the experimental reactors. Considering the ratio of 1.4 $kg\,COD\,kg^{-1}$ VSS referred by Parker [10], it was assumed an initial biomass concentration of 9.8 $kg\,COD\,m^{-3}$, corresponding to 7 $g\,VSS\,L^{-1}$. This value was divided by the seven types of microorganisms considered in ADM1, giving a much higher proportion for the methanogenic species, since the biomass used had been collected in a full-scale industrial reactor treating EC effluent.

Table 4
Initial conditions used in ADM1 implementation

Component	Unit	Value
Amino acid degraders	$kg\,COD\,m^{-3}$	0.784
Sugar degraders	$kg\,COD\,m^{-3}$	0.784
LCFA degraders	$kg\,COD\,m^{-3}$	0.784
Valerate and butyrate degraders	$kg\,COD\,m^{-3}$	0.784
Propionate degraders	$kg\,COD\,m^{-3}$	0.784
Acetate degraders	$kg\,COD\,m^{-3}$	3.920
Hydrogen degraders	$kg\,COD\,m^{-3}$	1.960
Amino acids	$kg\,COD\,m^{-3}$	0
Acetate	$kg\,COD\,m^{-3}$	0.01
Butyrate	$kg\,COD\,m^{-3}$	0
Cations	$kg\,COD\,m^{-3}$	0.04
Hydrogen ions	$kg\,COD\,m^{-3}$	5.79E−08
Soluble inerts	$kg\,COD\,m^{-3}$	0.01
Inorganic nitrogen	M	0.01
Sugars	$kg\,COD\,m^{-3}$	0.01
Composites	$kg\,COD\,m^{-3}$	0
Particulate inerts	$kg\,COD\,m^{-3}$	0

2.4. Sensitivity analysis and parameter estimation

Although all parameters affect model outputs, their significance differ from one to another. Sensitivity analysis has been widely applied to reduce model complexity, to determine the significance of model parameters and to identify the dominant parameters [16]. After a first simulating period, a sensitivity analysis was performed to sCOD and acetate ion concentration (S_{ac_ion}) variables. This step was carried out to identify the most influential parameters on model behaviour, thus reducing the complexity of parameter estimation procedure. The sensitivities were quantified in terms of the absolute variation of measurable process variables under the relative perturbation of model parameters in their neighbourhood domain [17].

As the simulating feed was assumed as a lumped substrate, the parameter estimation is of special concern in assessing this particular substrate (EC) anaerobic degradation. The main objective of this procedure was to tune the kinetics of the lumped substrate. Correlation between parameters was estimated by two-parameter optimisation using the secant method implemented in the AQUASIM® [17]. Using the standard deviations given by secant method, confidence limits for parameters were calculated using Student's *t*-distribution using 55 samples for a 95% confidence level.

3. Results and discussion

3.1. Sensitivity analysis

In general, the sensitivity analysis permitted the identification of the most important parameters on the system's dynamic behaviour. For the relative sensitivity analysis, a reference value is required as a starting point for evaluation the perturbation factor [16]. Since the earlier simulations did not produced high discrepancies between experimental data and predictions (generally lower than 20%), the original parameters were not changed.

The mean values of the absolute-relative functions, which express the magnitude of parameter effects, are presented in Table 5. Following the recommendations of the IWA Task Group, the several parameters were grouped into three classes accordingly

Table 5
Mean values of the sensitivity functions of variables to parameters

Rank	Variable			
	sCOD		S_{ac_ion}	
1	km_ac	8.01E−02	km_ac	7.97E−02
2	Y_ac	7.05E−02	Y_ac	7.02E−02
3	Ks_ac	5.52E−02	Ks_ac	5.50E−02
4	kdec_xac	2.14E−04	kdec_xac	2.13E−02

to their magnitude. Only the higher sensitivity parameters for each variable are here presented and those were considered for further estimation. Other parameters, with low sensitivity on model output, have been applied without any modification to the original values presented in Batstone et al. [9]. Both variables are strongly affected by the parameters related with the acetate degradation: maximum uptake rate (km_ac), yield of acetoclastic biomass (Y_ac) and half-saturation constant (Ks_ac). Sensitivities provided by other parameters (stoichiometric, disintegration and hydrolysis parameters) are not remarkable since the effluent used in the experiment did not contained solid materials. As it would be expected, the model revealed high sensitivity mainly to acetate related kinetics, since it accounted for an influent with substrate lumped as acetate. The experimental data used for fitting was achieved with the real effluent (EC containing not only acetate), so kinetic parameters chosen for estimation will reflect the behaviour of EC degradation rather than pure acetate degradation.

The shapes of sensitivity functions of variables with respect to maximum uptake rate (k_m) and half-saturation constant (K_s) are quite similar (not shown), leading to deduce high correlation between estimates of these parameters which makes both constants poorly identifiable from experimental data. In fact, any change in calculated values of the variables under study caused by a change in one of the parameters can be compensated by an appropriate change in the other one [17]. However, these are the constants with the highest impact among all the parameters, being usually chosen for estimation in the majority of studies using ADM1, such as Tartakovsky et al. [16] and Batstone et al. [15].

3.2. Model calibration

Based on the results of the sensitivity analysis, it was decided to estimate only the kinetic parameters related with the lumped substrate (K_s and k_m). The first step was to set the initial values proposed by the ADM1 report [9]. Then an iterative method was applied to adjust the most sensitive parameters until minimising the differences between the ADM1 outputs and the experimental data from SC1 assay. In particular, the estimation procedure used sCOD, methane flow, and S_{ac_ion} experimental series.

For estimation purpose, the secant method algorithm included in AQUASIM® was used. After six iterations the parameters were successfully tuned, as stated in Table 6. Correlation between k_m and K_s was of 0.96, which reveals linear dependency, although it is lower than that achieved by Batstone et al. [15] (0.98).

New simulations of reactor SC1 were then performed using these new values. Fig. 1a represents the experimental data for

Table 6
Initial and estimated parameter values (value ± confidence limit[a])

Parameter	Description	Initial value[b]	Final value	Unit
k_m	Maximum uptake rate	8	13.2 ± 0.48	d^{-1}
K_s	Half-saturation constant	0.150	0.060 ± 0.026	kg COD m^{-3}

[a] Confidence limit calculated using Student's *t*-distribution for 55 samples at a confidence level of 95%.
[b] Values for acetate from Batstone et al. [9].

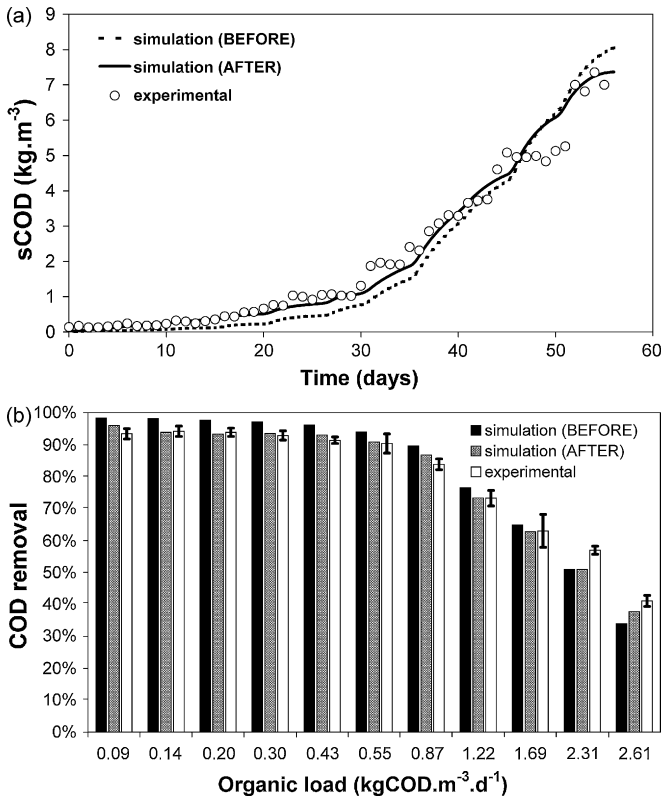

Fig. 1. Comparison between simulations and experimental data for reactor SC1 before and after parameter estimation: (a) soluble COD and (b) COD removal efficiency.

the evolution of sCOD inside the SC1 reactor as well as its simulations before and after parameter estimation. In general, it can be seen that the parameter tuning better approached the simulation to the experimental data, in particular under low OLR, up to 0.55 kg COD m^{-3} d^{-1} (30 days). However, under the highest loading conditions (2.31 and 2.61 kg COD m^{-3} d^{-1}), the model tends to overpredict the sCOD and thus it slightly underestimates the COD removal. Moreover, the model reveals that, at the operational conditions tested (increase of the OLR each 5 days), sCOD does not present steady trends during all simulating period for SC1 scenario, even during low OLR. This fact was more notorious for OLR above 0.87 kg COD m^{-3} d^{-1} (period after 35 days).

For a better understanding of the comparison between experimental data and model predictions, before and after parameter tuning, Fig. 1b presents the COD removal rates as a function of the applied organic load to SC1 reactor, calculated as the arithmetic average of the experimental values obtained for each OLR applied. The error bars represent one standard deviation unit from experimental records. Reporting to this figure it can be observed that, increasing the load up to 0.55 kg COD m^{-3} d^{-1} did not significantly affect the organic matter removal, which was always higher than 90%. After this OLR there is an effective drop on the COD removal, which can be interpreted as a substrate inhibition. Xing et al. [18] refer that, if a substrate pulse is applied to the anaerobic system before it has completely recovered from an inhibitory impact, a subsequent deterioration in reactor performance can be expected, and this is what can be observed on the subsequent loading rates.

Comparing the simulated scenarios before and after parameter estimation, it can be seen that the model tuning permitted the decrease of deviations to the experimental series, excluding the load 2.31 kg COD m^{-3} d^{-1} where deviation was about of 11% and out of the experimental standard deviation. With this exception,

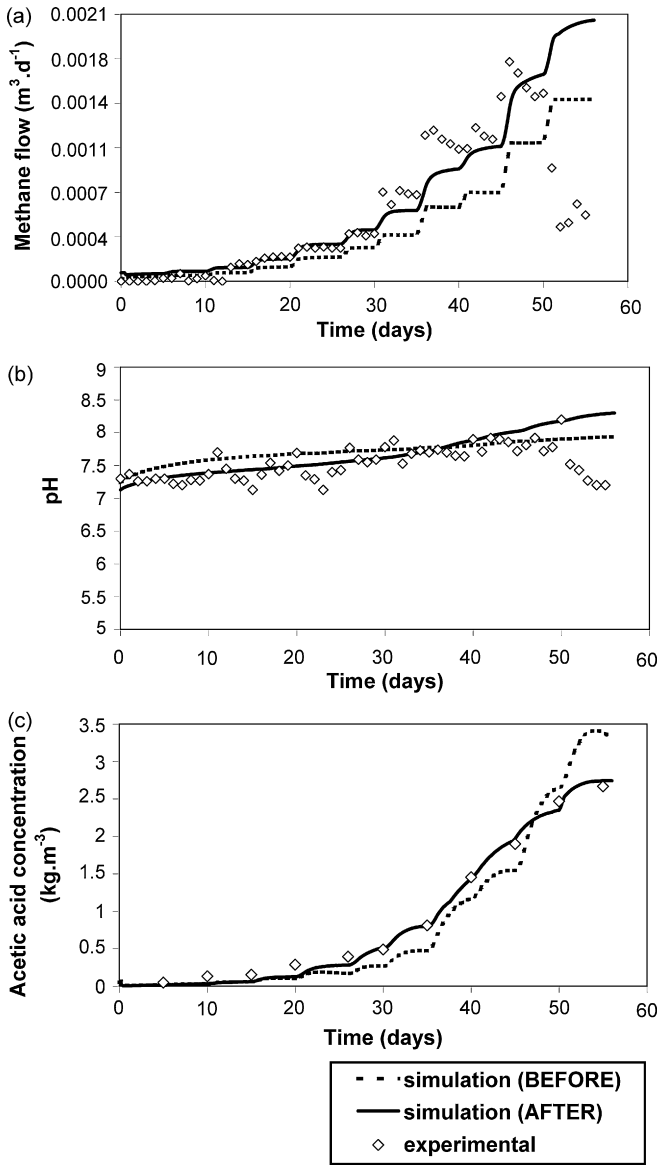

Fig. 2. Comparison between simulations and experimental data for reactor SC1 before and after parameter estimation: (a) methane flow; (b) pH; (c) acetic acid concentration.

simulation of the COD removal after parameter fitting showed lower relative errors, between 0.1 and 8.2%, against 2.9 and 17.4% for the simulation without parameter estimation. On the majority of the assessed OLR, the adjusted model successfully led to predictions within one standard deviation of experimental data, being also evident that the model accurately confirmed the COD removal efficiency drop under high loads.

Fig. 2a shows the evolution of methane production as a function of time, for the simulated data and the SC1 experimental series. Methane production was used instead of total biogas production because CO_2 or H_2O components do not directly relate efficiency removals, but rather changes in physicochemical system [11]. Reporting to the experimental observations, a steady response is more visible under low OLR, until 0.55 kg COD m^{-3} d^{-1} (days 25–30). After this point, the methanogenic activity reveals a transient behaviour, tending to a maximum value at the first day of the load increase. Indeed, steady behaviour of this variable was more difficult to achieve under loadings higher than 0.55 kg COD m^{-3} d^{-1}. This fact is consistent with the instability and COD removal decrease observed for this reactor during the higher loads. At the highest OLR applied (2.61 kg COD m^{-3} d^{-1}) there was an accentuated drop on methane production, which also suggests a high methanogenic inhibition by the substrate under this load.

The simulation of methane production in SC1 assay clearly predicts the occurrence of steady trends on the curve for each organic load applied, although it tends to deviate from experimental data after 30 days of running (OLR of 0.87 kg COD m^{-3} d^{-1}). Even after the parameter tuning, the simulation only predicted a better modelling quality under lower OLR, showing that it is impossible to describe methane production under low and high loadings simultaneously, using the same estimated parameters. Blumensaat and Keller [13] also reported that it was complicated to further optimise the parameter set, and therefore a complete match of simulated and experimental data for all loading conditions could not be obtained.

Besides this deviation for higher OLR, the model does not explain the sudden methane production drop under the highest OLR tested. This may probably be due to the kinetic issues that were not contemplated on ADM1 development, where Monod kinetic is assumed. Hence, it is necessary to do a screening study on EC biodegradation kinetics. On the other hand, the larger deviations in predicting methane production under medium and high OLR can also be explained with the non-optimisation of several parameters, for instance the application of the same and non-optimised gas transfer coefficients for different situations. In fact, gas transfer coefficients may differ in reality and the dependence on the specific process modelled has been neglected [13,19].

The experimental and simulated results for pH inside SC1 reactor are presented in Fig. 2b. Experimental data show some variability, maybe due to the alkali addition in a step increase with the organic load, when the feed was neutralised. In spite of better fitting after parameter estimation, the adjusted model did not answer to that experimental oscillation, maybe because it was difficult to simulate the equilibrium achieved after extra alkali addition when a pH drop was verified during the experiments. However, the prediction after parameter estimation matched the average trend of experimental series until day 46, corresponding to the beginning of load 2.31 kg COD m^{-3} d^{-1}. After this point, where more imbalances had happened, the simulated pH presents a rising trend that is not in agreement with the inhibition previously discussed under higher loads (methane production decrease), but in accordance with the simulation of other variables. Nevertheless, the pH was always kept under neutrality, so it did not cause additional inhibition.

Although the level of model outputs and analytical data correspond well, a further assessment of the pH modelling should be considered because, in this case, an ionic equilibrium is assumed in the liquid phase on the algebraic system formulation for S_{H+} calculation. Furthermore, the inhibition functions are discontinuous and so they can favour numerical instability in a stiff system such as ADM1 [20]. To face this problem, the development of ADM1 using all the ions as dynamic state variables was initially proposed by Rosen and Jeppsson [14] and should be an object for future research. The last developments on this specific calculation have been reported in studies such as Smith and Chen [21] and Zaher and Vanrolleghem [22], which proposed several procedures to solve the ionic equilibrium.

Fig. 2c presents the measured and simulated VFA evolution with time in SC1 assay. During the experimental trial, it was noticed that acetic acid was the only VFA present, thus only the simulation of acetic acid was considered in the VFA modelling. It can be observed that acetic acid simulation undertaken with tuned model predicted accurately the experimental behaviour of the SC1 reactor at the final stage before load increase, with exception for lower OLR where the acid accumulation was underestimated. This underprediction is in agreement with the overestimation of the effluent pH in this period,

as also stated by Parker [10]. The model also indicates that until day 35 of operation (OLR of 0.87 kg COD m^{-3} d^{-1}) there is a steady trend on acetic acid accumulation when the system is operated up to this OLR. After this load there was a very high increase on acetic acid accumulation that caused inhibition of the process as previously stated for the highest OLR applied. A remarkable fact is the prediction of the transposition of the stability limit of 2 g L^{-1} of acetic acid for the OLR of 2.31 kg COD m^{-3} d^{-1}. This transposition was experimentally observed for the two highest loadings, where severe inhibition problems occurred, which caused a decrease on COD removal and methane production. This value has also been widely reported as inhibitory [2].

3.3. Model validation

The validation step involves checking that the model responses generated during the model analysis agree with data obtained from a full-scale process. This is the ultimate check on the success of model building [7]. The validation here presented presupposes the model evaluation using independent data which has not been used for calibration purpose, such as the SC2 assay. In the absence of existing real data of the full-scale process, a significantly different scenario was assessed, which simultaneously permitted the assessment of the quality of the optimised model in predicting the experimental behaviour of EC anaerobic treatment and underline the benefits of molasses addition on the stability of the anaerobic treatment process for the highest loads. The model outputs were compared with measured data from the SC2 reactor operation, applying the same implementation previously described, setting the initial conditions as stated in Table 2 and without changing the previously optimised parameter set.

The comparison of model outputs for sCOD and experimental data are shown in Fig. 3a. Remarkably the model outputted the occurrence of flat trends of the curve for each OLR tested (simulating steady states) which were not previously predicted in the simulations of EC degradation in absence of co-substrate (SC1 assay), suggesting more stability for similar operating conditions. From Fig. 3a, the sCOD simulation accurately predicted the experimental behaviour for OLR up to 0.94 kg COD m^{-3} d^{-1}. For higher OLR (2.08 and 2.49 kg COD m^{-3} d^{-1}) the model overpredicted the sCOD inside the reactor and thus it underestimated the microbial acclimatation to the substrate. However, in spite of the peaks observed at the beginning of each high OLR, the model also predicted the recovery of treatment capacity, which is described by the drops after the load increase peaks. In general, a much better stability of COD removal was achieved in the presence of a co-substrate for similar conditions applied (up to OLR of 2.08 kg COD m^{-3} d^{-1}), and the model successfully predicted that. For the highest loading rates, it was only possible to predict a trend, which also confirms that it is not possible to obtain a complete match of simulated and experimental data for all loading conditions, which should be object of future research.

Fig. 2b and c shows the methane production and the methane content in the biogas, respectively, for the SC2 reactor. Once again, steady parts of the evolution curve for methane production (also suggesting steady states) were predicted by simulation for each load, although slightly overestimated, which also suggests a higher stability of the overall process. Both the methane production and its percentage in the biogas were predicted accurately for OLR up to 0.94 kg COD m^{-3} d^{-1}. The model also simulates a small overload situation when the load is increased from low to medium (0.29–0.94 kg COD m^{-3} d^{-1}), with the decrease in the methane content in the biogas from 80 to around 60%. The model could also predict the decrease on the methane content in the biogas at day 17, corresponding to the beginning of the OLR of 2.08 kg COD m^{-3} d^{-1}.

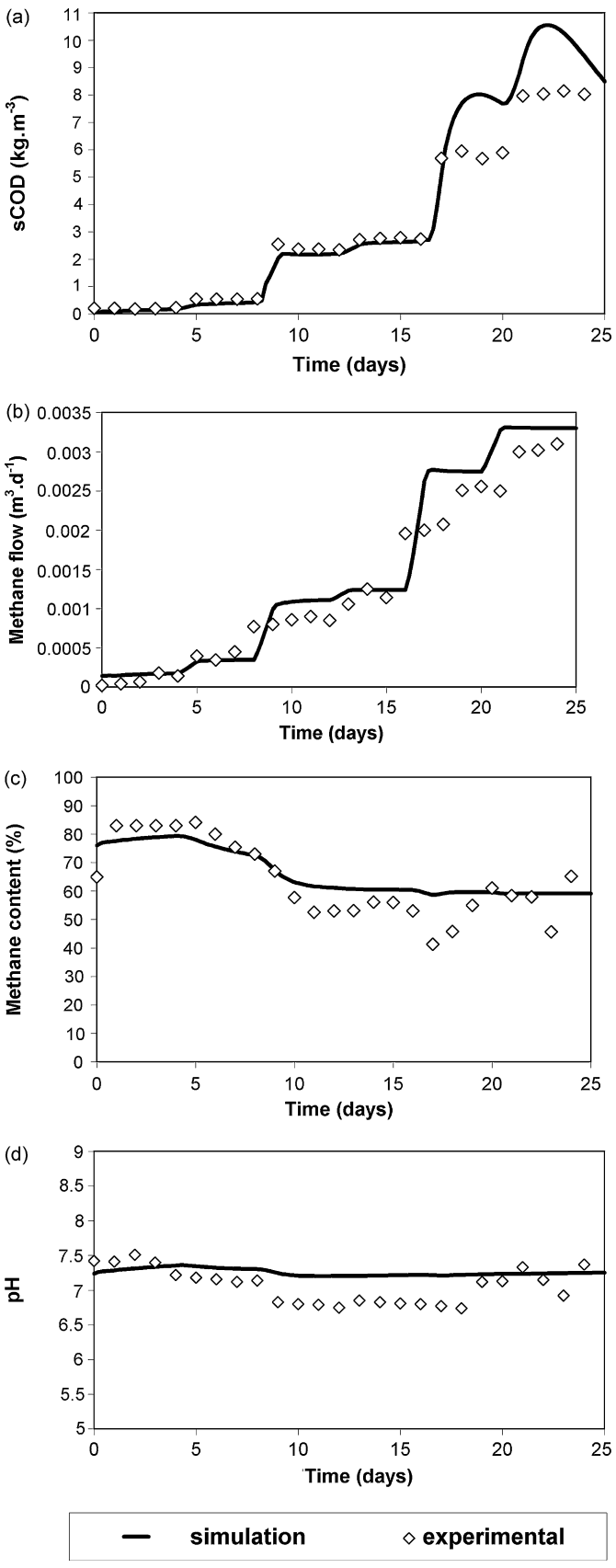

Fig. 3. Validation of simulations with experimental results of reactor SC2: (a) soluble COD; (b) methane flow; (c) methane content; (d) pH.

However, at the highest loadings (2.08 and 2.49 kg COD m^{-3} d^{-1}) the accuracy of model predictions decreased, which is in agreement with what happened with the COD removal. It is important to note that the methane production did not decrease at the highest loading as it happened in the reactor with only EC effluent, suggesting a much lower inhibition by the substrate itself. So, the failure of an overloaded reactor can be postponed if molasses addition is used.

Fig. 3d presents pH evolution and it can be seen that it did not present oscillations as the ones verified for reactor SC1 (Fig. 2b), which also shows a much better stability of the process for the same organic loads applied. It was not necessary to add extra alkaline solution for pH control as it happened with SC1 reactor.

The deviations in predicting the biogas production and quality found for the experiments at higher loadings, similarly to what happened in the model calibration using just EC effluent, can also be explained with the application of identical and non-optimised gas transfer coefficients for all situations. However, the model predicts the improvement on the process stability that has been also observed in the lab experiments with the addition of molasses, which helped to avoid the accumulation of toxic substrates and VFA inside the reactor. The present study for EC treatment using the saccharide addition permits the development of strategies, which may improve the stability of the real operation at a full-scale reactor at higher loading rates of 2–2.5 kg COD m^{-3} d^{-1}.

In addition, the deviations between experimental and simulated data may also be due to the fact that ADM1 differential equations are non-linear. Therefore, it was difficult to optimise all the sensitive parameters by adjusting simulation outputs with all the experimental results without making some discrepancy by any parameter identification method [19]. Another inconsistency between simulations and experimental results may be due to the correlation of some sensitive parameters with feed components. More detailed data for the process would reduce the influence of outliers. It should be noted that ADM1 have been criticised for requiring a detailed substrate definition [23].

4. Conclusions

The ADM1 was successfully implemented to simulate the EC anaerobic treatment in semi-continuous mode, under dynamic conditions. This model was able to yield similar results as found in experimental trials, either with or without the addition of an external carbon source. Furthermore, sensitivity analysis showed that the parameters k_m and K_s related with the degradation of the lumped substrate were the most sensitive, and were further adjusted (k_m = 13.2 d^{-1}; K_s = 0.06 kg COD m^{-3}).

Even though the model might not consider the methanogenic inhibition at an OLR of 2–2.5 kg COD m^{-3} d^{-1}, it proved the beneficial effect provided by the presence of the saccharide on stability and performance of the anaerobic system, which led to higher COD efficiencies and methane production. The implemented model satisfactorily described sCOD and thus the treatment efficiency of the reactors under different OLR. For the reactor with just EC effluent, the model addresses the difficulty in achieving steady states on COD evolution curve at each tested condition, being this effect quite pronounced under high OLR (higher than 1 kg COD m^{-3} d^{-1}), where stability problems occurred. In the case of the reactor containing molasses addition, a much better stability during all experiment was observed for this variable (occurrence of flat parts for each load applied), and the model predicted that very well, which proven the beneficial effect of molasses addition. The simulations tend to underpredict slightly the COD removal rates for operation under higher OLR, suggesting that it was unable to predict adaptation of the biomass to the substrate.

VFA simulation was well predicted for the majority of the steady states of the SC1 assay, while the pH was only accurately predicted up to OLR of 2 kg COD m^{-3} d^{-1}, addressing the difficulty on the ion equilibrium modelling task, also reported in other studies. The methane flow simulation predicted the occurrence of steady behaviour in each of the tested OLR, either without or with an external carbon source addition. However, for an OLR of 0.87 kg COD m^{-3} d^{-1} or higher without molasses, and 2 kg COD m^{-3} d^{-1} or higher with molasses, the simulations did not predict the difficulty to reach steady states for methane production, as well as its accentuated drop at the highest load in SC1 reactor.

The main deviations between predictions and experimental data were observed when the same model running is used for simulating operations at low and high OLR. These inconsistencies may be due to the identification and validity of all the sensitive parameters for different OLR and were the major drawback of ADM1 application. Nevertheless, these results illustrate that a high accuracy of all model predictions is not always required, as only a limited number of simulation outputs are of relevance, and the accuracy of these can be estimated quite well with some particular parameter estimations. This study underlined the need of good parameter estimation to adequately predict the behaviour of this particular anaerobic process under different OLR. The fundamentals of the model are generally valid, although further studies would be needed to accurately validate the model on existing full-scale data. The interesting topics for future research include studies of kinetic mechanisms for biodegradation of the evaporator condensate, which may differ from Monod kinetics, and their further integration into ADM1.

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