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Initial rates technique as a procedure to predict the anaerobic digester operation

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ABSTRACT

In this study a novel and practical procedure was developed, that involves: initial methane production rate measurement in batch tests, kinetic parameters determination and modeling application in a continuous digester. The procedure was evaluated with three experimental conditions: raw sludge as substrate incubated at 35 °C and 55 °C and thermal pretreated sludge incubated at 35 °C. The initial specific methane production rate was fitted with the Monod type equation in order to calculate the kinetic parameters. The values obtained for the maximum specific methane production rate were 0.043, 0.143 and 0.052 $gCH_4\,gVS_I^{-1}\,d^{-1}$ for each experimental condition, aforementioned. The substantial increment of this parameter at thermophilic condition shows the differences in the specific maximum growth rate between thermophilic and mesophilic populations. The affinity constant values were 3.842, 4.790 and 4.623 $g\,L^{-1}$ for each experimental condition; however, a significant uncertainty was obtained due to some identification problems. A preliminary validation of the procedure was applied for predicting the operation of a continuous digester treating raw sewage sludge. The overall behavior of the system was represented by the model, although it slightly underestimates the experimental values, by approximately 20%. The results achieved, indicate that the procedure may be used as a tool in a real scale operation; however, further research must be performed.

1. Introduction

Anaerobic digestion has remarkable advantages to stabilize sewage sludge: low energy consumption (because aeration is not required), less sludge production than in the aerobic process and biogas is produced, which can be exploited as a source of renewable energy. Biogas from anaerobic digestion is considered an important renewable energy source for Europe with a total annual potential estimated in excess of 200 billions m^3 [1].

In the anaerobic degradation of sewage sludge, large hydraulic retention times (HRT) are normally used (20–30 days) in order to ensure a significant reduction of solids from the influent. However, the readily biodegradable organic fraction presents in the influent is responsible for an important percentage of the biogas generated daily, being the methanization of the solids like a noise behind the main flow of biogas [2]. In this context, recent research has focused on the increment of the readily organic fraction (which has been commonly associated with the soluble organic fraction) of the sewage sludge, for instance the implementation of pretreatments techniques [3].

The Biochemical Methane Potential (BMP) test [4] represents the conventional procedure to evaluate anaerobic biodegradability of any substrate fed into anaerobic digesters. This method is considered simple, reliable and allows the estimation of some important kinetic parameters [2]. There are two main drawbacks of this method. Firstly, only the biogas can be measured continuously in order to maintain the technical and economic feasibility of the method. Secondly, this process is carried out in batch mode, despite the fact that most anaerobic reactors operate in continuous mode. The latter represents a serious issue since in batch tests all the compounds are in a dynamic state, and some of them might exert an unexpected and unconsidered effect on the biomass behavior [5]. Therefore, the use of kinetic parameters determined through batch testing should be taken carefully and only as a first approximation for its application in a continuous digester [2,6].

The initial rate reaction measurement, which has been widely applied in enzymatic processes, is used to obtain either production or consumption rate of a specific compound involved in a reaction, minimizing the effect of the dynamic conditions, for instance, the inhibition by product or substrate limitations [7]. Substrate depletion or product build-up can be used for the evaluation of the initial rate (if the reaction stoichiometry is well-known). Few studies have reported the use of this method in anaerobic digestion, Donoso-Bravo et al. [8] evaluated the influence of the temperature on the main reactions of the anaerobic digestion, and Flotats et al. [9] esti-

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Nomenclature

S	substrate concentration (measured of g of VS fed)
X	anaerobic biomass (measured of g of VS inoculated)
ξ	state variable
D	dilution rate (d^{-1})
r	reaction rate ($g L^{-1} d^{-1}$)
μ	specific growth rate of the anaerobic biomass (d^{-1})
μ_m	maximum specific growth rate of the anaerobic biomass (d^{-1})
Ks	affinity constant ($g L^{-1}$)
K_0	yield coefficient for organic matter degradation ($g g^{-1}$)
K_1	yield coefficient for methane production ($g g^{-1}$)
K_2	yield coefficient for carbon dioxide production ($g g^{-1}$)
q_{CH_4}	biogas production rate ($gCH_4 d^{-1}$)
Ri	initial methane production rate ($gCH_4 gVS_F^{-1} d^{-1}$)
Ri_x	initial specific methane production rate ($gCH_4 gVS_I^{-1} d^{-1}$)
ν_m	maximum production rate of methane ($gCH_4 g_x^{-1} d^{-1}$)
t	time (d)
J	objective cost function
η_{exp}	experimental value
η_{mod}	simulated value
p	group of parameters to be determined
N	number of measurements
gVS_F	g of VS fed
gVS_I	g of VS inoculated

mated kinetic parameters of the gelatine anaerobic degradation, both using the initial rate technique.

The aim of this study was to develop a rapid and practical experimental procedure to estimate kinetic parameters from the anaerobic digestion of sewage sludge, based on the initial rate technique, and to evaluate its applicability for predicting the behavior of an anaerobic continuous-digester.

2. Materials and methods

2.1. Experimental set-up

Batch experiments, in triplicate, were run in glass serum bottles with a effective volume of 100 ml (160 ml of total volume). Biogas production was measured manually by a pressure transmitter (Druck, PTX 1400, range 1 bar). Three different experimental conditions were evaluated: experiment 1: Raw secondary sludge (RSS), $73.26 \pm 4.50\ gTS\ L^{-1}$ and $53.69 \pm 5.33\ gVS\ L^{-1}$ as substrate incubated at mesophilic condition, experiment 2: Thermal pretreated secondary sludge (ThPSS), obtained as it is described in [10], $47.87 \pm 3.81\ gTS\ L^{-1}$ and $35.6 \pm 3.6\ gVS\ L^{-1}$ as substrate incubated at mesophilic condition and, experiment 3: Raw secondary sludge as substrate at thermophilic condition. For all the experiments the secondary sludge that was used came from the wastewater treatment plant (WWTP) of Valladolid, Spain (233,000 p.e.). Mesophilic and thermophilic experiments were carried out at 35 and $55\,^{\circ}C \pm 0.6\,^{\circ}C$, respectively, in a thermostatic room. Anaerobic sludge was used as the inoculum for the anaerobic tests, which was obtained from pilot-scale mesophilic ($25.50 \pm 1.68\ gTS\ L^{-1}$ and $12.57 \pm 0.73\ gVS\ L{-}^{1}$) and thermophilic ($25.06 \pm 0.85\ gTS\ L^{-1}$ and $12.76 \pm 0.63\ gVS\ L^{-1}$) anaerobic digesters, which were fed with mixed waste-activated sludge (from the same WWTP). Furthermore, $1\ ml\ L^{-1}$ of macro-, micro-nutrients and $1\ g\ L^{-1}$ of sodium bicarbonate were added in all assays in order to supply the necessary elements and enough alkalinity to maintain the pH above 7.

2.2. Linear fed/inoculum ratio (F/I) determination

The initial slope of the biogas production curve must be proportional to the biomass concentration, therefore, the biomass concentration should be properly diluted to attain a linear product concentration (biogas in our case) versus time relationship within a reasonable assay time [7]. Thus, prior to the initial rate test, a proper range of F/I has to be determined in order to only evaluate the effect of the substrate concentration. To estimate this F/I range, the initial methane production rate (Ri) (as $gCH_4\ gVS_F^{-1}\ d^{-1}$) is determined from anaerobic batch tests using several biomass concentrations, keeping a constant substrate concentration. Hence, the linear F/I range may be estimated when the variation of the initial methane production rate (Ri) tallies with the variation of biomass concentration.

2.3. Initial rate of methane production

Five substrate concentrations for all the experiments (in triplicate) were assessed to calculate the initial specific methane production rate (Ri_x) ($gCH_4\ gVS_I^{-1}\ d^{-1}$). The initial rate was estimated from the maximum slope (linear regression) between the methane produced and time. Biogas production was measured manually using a pressure transmitter (Druck, PTX 1400, range 1 bar) which was placed in the head space of each batch system. After each daily pressure measurement, the biogas in the head space was released, which reduced the pressure in the head space to atmospheric pressure. Biogas composition was measured by gas chromatography through the direct injection of 1 mL of sample into the column.

2.4. Kinetic parameters determination

A global kinetic model of the anaerobic digestion process was considered (Eq. (1)). These types of models, which have been used in the anaerobic degradation of several substrates [11,12], are useful for control or design purposes, and they may be more easily managed than complex ones. The relationship between the specific growth rate of the anaerobic biomass and the substrate concentration might be well-represented by a Monod kinetic (Eq. (2)).

$$K_0 S \xrightarrow{r} X + K_1 CH_4 + K_2 CO_2 \quad (1)$$

$$r = \mu_m \frac{S}{Ks + S} X \quad (2)$$

Methane, as a primary metabolite of the growth, can be related to the reaction rate by means of a stoichiometric coefficient (Eq. (3)).

$$q_{CH_4} = K_1\, r = K_1\, \mu_m \frac{S}{Ks + S} X \quad (3)$$

The biomass concentration (X) in anaerobic digestion is quite difficult to measure and there is no clear consensus how it should be estimated [13]. However, if the slow growth of the anaerobic population and the short length of the initial rate test (about 3 days) are considered, it can be assumed that the biomass concentration should remain approximately constant, and on the other hand, K_1 and μ_m are lumped, Eq. (3) can be modified to obtain:

$$\frac{q_{CH_4}}{X} = Ri_x = \nu_m \frac{S}{Ks + S} \quad (4)$$

The maximum production rate of methane (ν_m) represents the maximum theoretical value valid for the biomass and substrates that are being evaluated.

Thereby, the set of data of initial methane production rate, Ri_x, at different initial substrate concentrations is used for the estimation of both kinetic parameters (ν_m and Ks). Nonlinear curve-fitting using lsqcurvefit (optimization toolbox in Matlab® 7.0), which uses the least squares procedure, was applied to calculate the unknown parameters (Eq. (5)), which measures the difference between the experimental measurements and the corresponding simulated value. It is necessary to point out that other studies, usually, estimate the parameters values after a model linearization (for instance Lineweaver–Burk plot), however these methods have a significant drawback since the error is unevenly distributed [7].

$$J(p) = \min \sum_{t=1}^{N} (\eta_{\exp}(S) - \eta_{\mathrm{mod}}(S,p))^2 \quad (5)$$

In order to obtain information about the accuracy of the estimated kinetic parameter, the covariance matrix associated with each set of optimal parameters and the matrix correlation were calculated as in reference [14].

2.5. Preliminary validation of the model and the procedure

The estimation of the stoichiometric coefficients, as well as, the cross-validation of the model and the estimated kinetic parameters, were performed by using data from a pilot-scale anaerobic reactor. This reactor (194 L of effective volume) was operated at 35 °C for 62 days and was fed with secondary sewage sludge from the same WWTP than the one used in the initial rate test (experiments 1 and 2). The average composition of the raw sludge was as follows: TS $52.2 \pm 6.5\,\mathrm{g\,L^{-1}}$, VS $36.2 \pm 4.5\,\mathrm{g\,L^{-1}}$, total COD $53.1 \pm 2.7\,\mathrm{g\,L^{-1}}$ and soluble COD $2.8 \pm 1.3\,\mathrm{g\,L^{-1}}$. The reactor was completely mixed by liquid recycle. The first 35 days of operation, in which an increasing sewage sludge flow was applied, were used for the estimation of the stoichiometric coefficient (K_0, K_1 and K_2) and the initial conditions (biomass and substrate concentration). This calibration process was carried out by using nonlinear optimization (fminsearchbnd in Matlab7.0®), through a minimization of the sum of the least squares between model and measured outputs (Eq. (5)). The following 27 days were used for the validation of the model. The model for a continuous digester, taking into account model described in Eq. (1), might be described in a general matrix form:

$$\frac{d\xi}{dt} = D(\xi_i - \xi) + Kr(\xi) \quad (6)$$

where

$$\xi = \begin{bmatrix} X \\ S \end{bmatrix}, \qquad \xi_i = \begin{bmatrix} 0 \\ S_0 \end{bmatrix}, \qquad K = \begin{bmatrix} 1/K_1 \\ -K_0/K_1 \end{bmatrix},$$

$$r(\xi) = \left[\nu_m \frac{S}{\mathrm{Ks} + S} \right]$$

This simple approach assumes that all the gas goes out from the reactor due to the low solubility of the methane in the liquid and so with the CO_2 flow. The generated CO_2 that exits the reactor depends on the pH in the reactor. This variable was maintained in a narrow range between 7.70 ± 0.17; thus the CO_2 dissolved in the liquid could be neglected.

3. Results and discussion

3.1. F/I range determination

The cumulative methane production during 3 days of operation for all experimental conditions is shown in Fig. 1A, C and E, respectively. As expected, increasing methane production rates were observed as the F/I ratio decreased, for all conditions. This may be due to the fact that more biomass is available to degrade the organic matter at low F/Is. All the linear regressions were well correlated, with correlation coefficients R^2 always greater than 0.99.

Fig. 1B, D and F shows the percentages of reduction of the initial methane rate production (Ri) with respect to the F/I ranges evaluated, for each experimental condition. These bars graph represent the variation (in this case only reduction) of the biomass concentration (which were used to set different F/I ratios) and the initial production rate, for the respective F/I ratio. As it was previously mentioned, the linear F/I range may be estimated when the variation of Ri, roughly, matches with the variation of biomass concentration. In the experiment 1 and 2 (RSS and ThPSS at mesophilic temperature), the linear range is observed within similar values 0.51–1.04 and 0.56–1.11 $\mathrm{gVS_F\,gVS_I}^{-1}$, results that are comparable to those obtained in other studies [15,16]. In the case of experiment 3, the linear F/I range is slightly wider, between 0.71 and 1.41 $\mathrm{gVS_F\,gVS_I}^{-1}$. Hence, the initial rate tests were carried out within these ranges.

3.2. Initial rate calculation and kinetic parameter estimation

Fig. 2 shows the methane accumulated profile during the assay at several initial concentrations of RSS (experiment 1, Fig. 2A) and ThPSS (experiment 2, Fig. 2B) and RSS (experiment 3, Fig. 2C). An increasing methane production rate was observed at increasing initial substrate concentrations. A small increment in the initial production rate was observed at similar concentrations, comparing experiment 2 with 1, which indicates the kinetic importance of the presence of a high fraction of soluble organic matter. In the case of experiment 3, the initial slopes, for all the initial substrate concentrations, were notably more pronounced than those obtained in the mesophilic experiments, which denotes that thermophilic biomass can uptake the organic matter much faster than mesophilic biomass. The standard deviations for all the samples were small (in many cases negligible), thus, each curve was clearly different from each other. In each figure, an inset table with the results of the initial methane rate production calculation was placed. These data, i.e., the initial methane production rate and the initial substrate concentrations, were fitted with the Monod-type equation (Fig. 3). A quite acceptable agreement between the data and the model can be noticed for all the cases, which indicates that the methane production rate behavior can be described by Monod kinetic. The obtained values of ν_m and Ks were: experiment 1, $0.043 \pm 0.001\,\mathrm{gCH_4\,gVS_I}^{-1}\,\mathrm{d}^{-1}$ and $3.842 \pm 0.685\,\mathrm{g\,L^{-1}}$; experiment 2: $0.052 \pm 0.002\,\mathrm{gCH_4\,gVS_I}^{-1}\,\mathrm{d}^{-1}$ and $4.623 \pm 1.020\,\mathrm{g\,L^{-1}}$; experiment 3: $0.143 \pm 0.010\,\mathrm{gCH_4\,gVS_I}^{-1}\,\mathrm{d}^{-1}$ and $4.790 \pm 0.965\,\mathrm{g\,L^{-1}}$

An increase of 20% in the value of ν_m, with respect to the experiment 1, was observed when ThPSS was used as substrate (experiment 2), which is explained because more soluble organic matter is available at the beginning of the degradation process. These results may explain in part why thermal hydrolysis, as pretreatment of RSS, improves the methane production in anaerobic digesters, which has been normally reported roughly between 15% and 25% [17]. On the other hand, an important increment of this parameter was observed under thermophilic conditions (experiment 3) compared with experiment 1 (around 230%). This accentuated increment explains the difference in the specific maximum growth rate between thermophilic and mesophilic populations, such as it has been reported in other studies [18,19]. The latter is what makes it possible to operate anaerobic thermophilic reactors at a lower HRT [20].

With regards to Ks, the values obtained are similar to those obtained by Tomei et al. [15] and Sötemann et al. [21] who used the Michaelis–Menten model to evaluate the hydrolysis reaction in the anaerobic degradation of sewage sludge under mesophilic conditions. The dispersion of the values are greater than those obtained for ν_m since the standard deviation is roughly 20% of the aver-

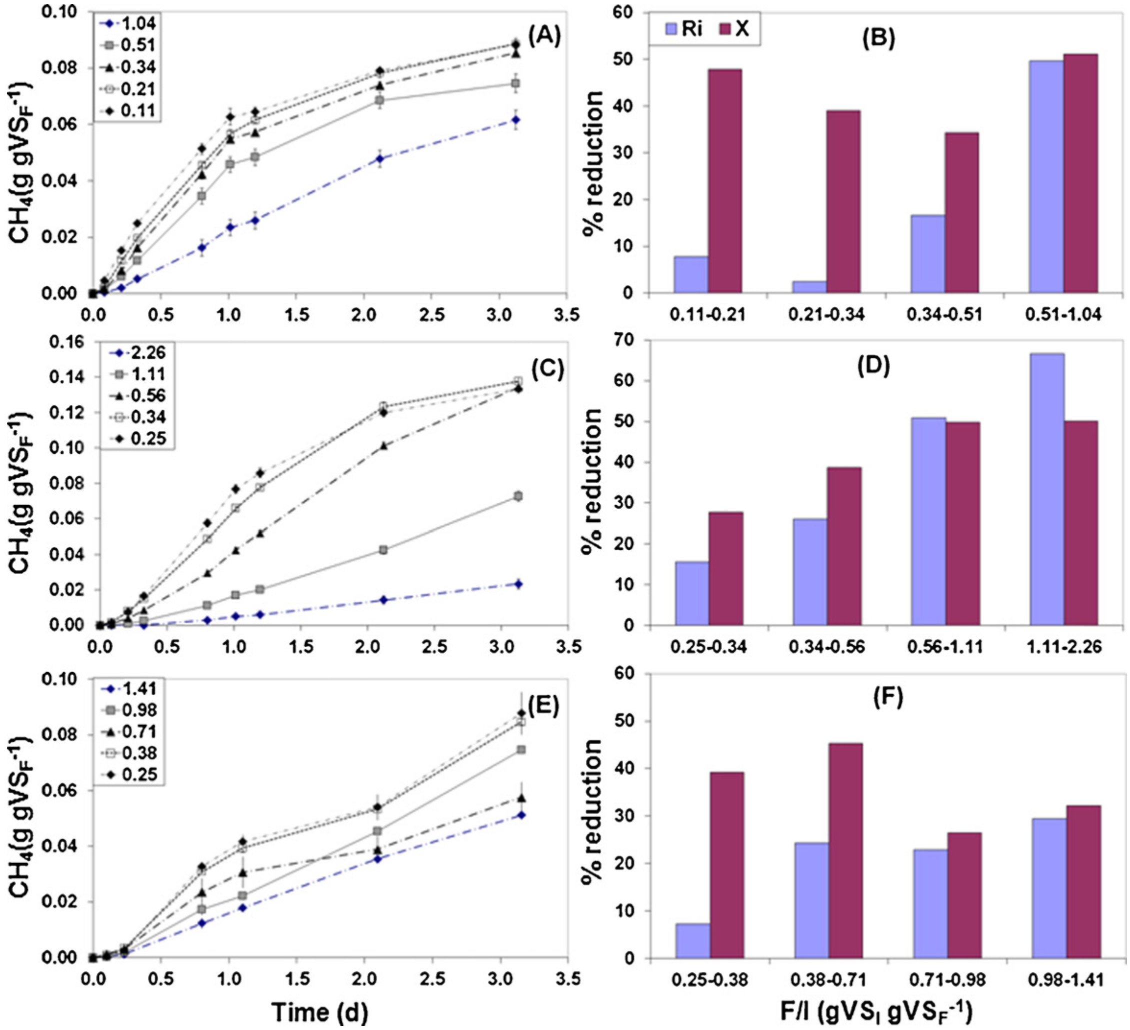

Fig. 1. Tests for F/I determination. (A, C and E): biogas production profiles and (B, D and F): percentages of reduction of *Ri* and *X* with respect to the F/I ranges evaluated for experiments 1, 2, and 3, respectively.

age values of the parameter. Furthermore, the pair of parameters presents a correlation at a degree of 0.69, which shows that there is an important correlation between them; however, slightly less than the correlation values found by Flotats et al. [22] and Haag et al. [23]. In this sense, several studies have reported identification problems in the determination of the Monod parameter, which commonly occurs when either a limited number of data points are available [24] or the concentration of the substrate does not cover a wide range of values [25]. Similar identification difficulties with Monod equation have been observed in even more controlled experiments in which biomass and substrate measurements were performed [26]. In any case, the results obtained show that the thermophilic biomass needs approximately the same substrate concentration to reach the maximum methane production rate, which is 4-fold greater than the one obtained for mesophilic biomass. Hence, thermophilic population seems to have a much better affinity for the same substrate.

3.3. Application in a continuous reactor

Fig. 4 shows the operation of the anaerobic pilot digester and the calibration/validation of the model, using data of CH_4 and CO_2 flows. The first part of the data was used for the determination of the set of stoichiometric coefficients and the initial conditions for the biomass and substrate concentration. As a result of the calibration the following stoichiometric coefficient were estimated: $K_0 = 4.262\,\mathrm{gVS\,gVS_I^{-1}}$, $K_1 = 3.68 \times 10^{-4}\,\mathrm{gCH_4\,gVS_I^{-1}}$, $K_2 = 7.04 \times 10^{-4}\,\mathrm{gCO_2\,gVS_I^{-1}}$, $X_{(0)}$: 1.709 g L^{-1} and $S_{(0)}$: 7.484 g L^{-1}. The total residual variance of the calibration was 9.454 ($s = 3.07\,\mathrm{d^{-1}}$). From this, error bars were included since it can be estimated that the residuals are characterized in the same way as the measurements errors. The final values obtained of the state variables in the calibration process were used as the initial ones, for the next step.

To assess the quality of the estimated coefficient sets and the kinetic parameters determined from the initial rate method, a cross-validation study was undertaken. In Fig. 4B, the model outputs (CH_4 and CO_2) were compared with measured data from the pilot digester. In general, biogas production was underestimated by the model, following, however, the global trend of the behavior system. During day 37 and 40 there was a feeding problem because of a substrate depletion (Fig. 4A), which triggered a drop in the biogas flow. This reduction was well-represented by the model. Afterwards, the model shows a continuous increase of the biogas prediction after the feeding problem, although it slightly underestimates the experimental values, which may be due to some changes in the substrate or anaerobic biomass characteristics, or some variations in certain operational conditions that the model is not able to represent. This underestimation of the model was a little bit more significant in the case of the CH_4 flow, with an aver-

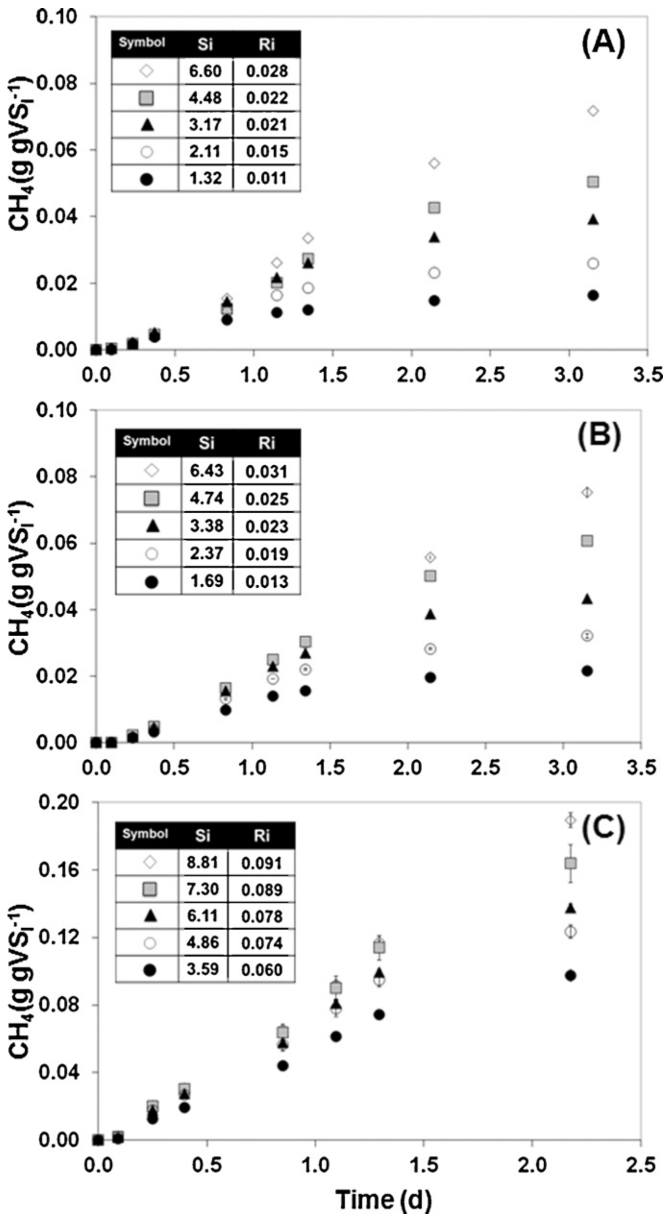

Fig. 2. Initial methane production at five initial substrates concentrations. (A), (B) and (C), experiment 1, 2 and 3, respectively. In inset table, Si initial substrate concentration and Ri_x initial methane production rate.

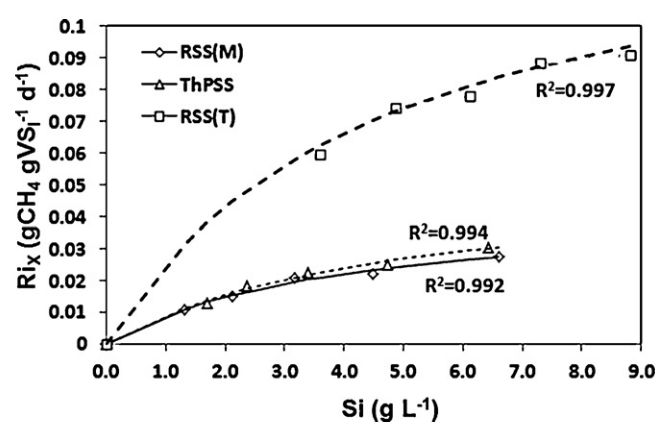

Fig. 3. Results of the model fit (Monod equation) with experimental data. RSS(M), raw sewage sludge incubated at 35 °C; ThPSS, Thermal pre-treated sewage sludge; RSS(T), raw sewage sludge incubated at 55 °C. Si: initial substrate concentration; Ri_x, initial methane production rate.

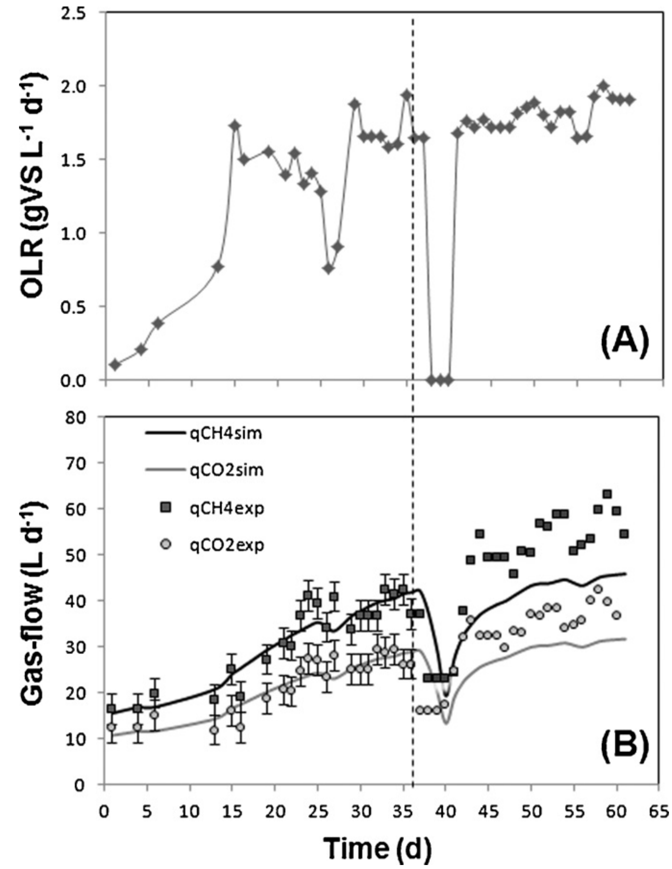

Fig. 4. Data from the operation of the anaerobic digester treating raw sewage sludge (RSS). (A) OLR applied and (B) Model calibration and validation.

age of 20.4 ± 5.7% less than the experimental values, whereas for the CO_2 the average was 16.7 ± 6.0%. Similar results were obtained by Batstone et al. [2], although underestimations around 50% in the prediction of the biogas production for two anaerobic digesters were observed, using kinetic parameters determined by BMP. In that study, a more accurate prediction of the digester was achieved by using kinetic parameters obtained using data from the continuous full-scale digester, in spite of that the estimation procedure to determine those parameters was more difficult than the one carried out with data from BMP test.

To assure the reproducibility of the procedure, the same substrate that is being treated by the continuous digester must be used as substrate in the initial test. Likewise, the same anaerobic biomass from the digester has to be used as the inoculum for the test. In addition and in order to improve for the prediction of the digester using this procedure, the initial rate test should be to perform regularly (monthly, for instance), which would allow to take into account the possible variations in the sewage sludge characteristics as well as the changes in the anaerobic biomass of the reactor.

Many studies employ anaerobic batch tests to determine some kinetic parameter; however this data should only be taken as a first approximation when they are applied in continuous digesters. Of course, plenty of other factors, such as: substrates characteristics, inoculum history, adaptation, etc., besides the conditions of the experiments (batch or continuous), may exert an important influence in the final result of the model prediction. However, the nature of the kinetic assay, which was the issue addressed in this study, is considered the major responsible in the variability of the kinetic parameters values [27]. The initial rate test may represent a proper tool for these purposes, although further research is required since these results show some promising results, these are just valid for the specific conditions under this study. In the case, for instance, when inhibitory or complex compounds are present in the substrate, the results may change substantially.

4. Conclusions

This experimental and mathematical procedure, here presented, may represent a novel technique to obtain kinetic parameters using both, the known and conventional set up of the BMP and the initial reaction rate concept. The main advantages of this procedure are: (1) only methane measurement is necessary, (2) the duration of the assay is about 3 days instead of 20 days of the BMP test, which makes this method easier to implement into a real-scale operation and for taking operational decisions, and (3) the kinetic parameters obtained are less influenced by the dynamic of the BMP test. The main drawbacks are (1) due to the lack of measured variables (CH_4) a very simple model must be used, which gives us a simplified understanding of the process and (2) Overloads, temperature and inhibition problems cannot be predicted. Nevertheless, as long as more variables such as VFA, SS, COD, etc., can be measured during the initial rate test, more kinetic parameters might be determined, increasing the model complexity and the knowledge of the system.

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