Modelling of the temperature-phased batch anaerobic digestion of raw sludge from an urban wastewater treatment plant

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ABSTRACT

The disposal of excess sludge from wastewater treatment plants is a serious problem that needs to be addressed. Temperature-phased anaerobic digestion (TPAD) which combines thermophilic and mesophilic processes in one, brings together the advantages of both systems. The aim of the present work was to develop a simple kinetic model to describe the TPAD of sewage sludge in batch completely stirred tank reactors (CSTRs) and to determine the kinetic parameters of both thermophilic and mesophilic stages. A zero-order kinetic equation described the thermophilic step after 2, 4 and 6 days of

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digestion time (experiment 1, 2 and 3, respectively), while a first-order equation was found to be adequate to correlate the methane gas accumulated with time in the mesophilic step, the kinetic constant being 0.21 days^{-1}. The methane yield coefficient obtained was found to be almost proportional to the digestion time used in the thermophilic step with values of 0.067, 0.132 and 0.193 L CH_4 STP/g VS_{added} for experiments 1, 2 and 3, respectively. By contrast, the kinetic constant of the mesophilic stage was not influenced by the digestion time used in the thermophilic phase.

Keywords: BMP (biochemical methane potential) assay; kinetics; sewage sludge; TPAD (temperature phased anaerobic digestion).

INTRODUCTION

Due to the enforcement of current regulations on management of biowastes as as sewage sludge[1], the number of municipal wastewater treatment plants (MWTPs) worldwide has increased considerably, which has lead to an improved environment. However, huge amounts of sewage sludge (an average 30 kg dry matter/inhabitant year) are generated [2], which must be stabilized before discharge because of its unstable, decomposable nature [3].

Therefore, the increasing production of sewage sludge is a serious concern worldwide [4]. Of the available technologies, anaerobic digestion (AD) is the most commonly used at medium and large MWTPs. By generating energy-rich biogas as methane (in excess of the level required for process operation) and yielding a nutrient-containing final product, [5] it has the ability to reduce the volume of sludge. However, its application has often been limited by foaming and low overall degradation efficiencies (30%–40%). The poor degradation of colloidal particles has resulted in long retention times (>20 days) in anaerobic processes [6].

Anaerobic treatment reactors are usually operated at mesophilic conditions in which better process stability can be achieved [7]. Although some studies have reported that thermophilic processes can tolerate higher organic loading rates (OLRs) and operate at shorter hydraulic retention times (HRT) while generating more biogas [8,9], they offer attractive advantages such as more volatile solids being destroyed, higher biogas generation, and less foaming over mesophilic plants. However, failure in temperature control may result in a biomass washout [10] with an accumulation of volatile fatty acid (VFA) due to the inhibition of the methanogenesis phase [8].

Therefore, temperature-phased anaerobic digestion (TPAD) which combines both temperatures (thermophilic and mesophilic) in the same process [11] brings together the advantages of both systems: it improves the reduction of solids and the production rate of biogas by enhancing the digestion rate limiting step, i.e. the hydrolysis of organic matter. Other beneficial features include the stabilisation of the sludge (the VFA generated under thermophilic conditions are degraded in the mesophilic reactor), the inactivation and reduction of pathogens (due to thermophilic temperatures which are adequate for preventing the reproduction of pathogens), and the improvement of sludge dewaterability. [12]

Although some studies have been carried out with the first reactor operating at mesophilic temperature and the second at thermophilic, [13,14] most configurations studied have been developed either with a thermophilic-mesophilic sequence [15-17] or with both sequences. [18]

Many researchers have proposed a solution by simulating anaerobic digestion processes. Early steady-state models assumed a rate-limiting step, and most of the developed models were necessarily complex, partial, and unstructured. The use of these models has been relatively scarce and limited in practice. Therefore, new models for anaerobic digestion processes are needed. In addition, the increasing complexity of advanced digestion technologies requires easily applicable models that can show the impact of changing environments on chemical and microbial species. [19]

Although TPAD sludge process has been studied over the last few years, there are few references in literature about TPAD kinetic modeling. [11,19-21] Most of the studies used the Anaerobic Digestion Model Nº1 (ADM1) [19-22] to fit data related to the semi-continuous process. This model [23] consisted of a number of processes to simulate all possible reactions occurring in anaerobic sludge including not only biological reactions, such as hydrolysis of suspended solids, growth and decay of microorganisms, but also physico-chemical reactions including ion association/dissociation and liquid-gas transfer. [19] In almost all cases the ADM1 model reflected the trends that were observed in the experimental data. However, the concentrations of VFAs were consistently over-predicted in digesters with short solid retention times (SRTs). [22] It would appear that the inhibition functions associated with low pH values tend to overestimate the impact of pH on biokinetic rates for the acid-consuming bacteria [22]. Moreover, it has been reported that some deviations in predicting biogas and composition when ADM1 was used to simulate the two-stage anaerobic digestion process of sewage sludge have been found [21]. In addition, this model has a critical disadvantage - many parameters [19,21] are very difficult to measure. Furthermore, in the case of anaerobic digestion, practical application is very limited due basically to the complexity of processes and to the high number of components involved in them.

On the other hand, it appears that no scientific works on modelling TPAD batch processes have been reported in the literature. Therefore, more knowledge about the kinetics of these kinds of processes needs to be obtained, because an understanding of the kinetics of the anaerobic digestion process enables predictions of the performance of digesters and assists in design. Kinetics can also contribute to the understanding of the mechanisms regulating biodegradation.

With this in mind, it would be interesting to develop and investigate the ability of a model to fit the experimental data obtained in a TPAD-BMP (biochemical methane potential) system. BMP or batch tests have been used as a quick and inexpensive method for determining the ultimate biodegradability and associated methane yield during the anaerobic fermentation of organic substrates. The biochemical methane potential assay is widely used to test the feasibility and degree of anaerobic digestion of different feedstocks. [24]

The aim of the present work was to develop a simple kinetic model and investigate its ability, to describe the TPAD of sewage sludge in batch CSTRs (completely stirred tank reactor), and to determine the kinetic parameters and the factors that could affect them. For this purpose, raw sludge samples derived from an urban wastewater treatment plant were subjected to anaerobic digestion assays in batch mode under thermophilic conditions (55 ºC), and afterwards another batch assay under mesophilic temperature (35 ºC).

MATERIALS AND METHODS

The experimental study was carried out in a multi-batch reactor system. The apparatus is composed of a bank of four stirred anaerobic reactors of 3 litres of the total volume and 2.5 litres of the working volume, which are heated using a thermostatic bath. The equipment has been fully described elsewhere. [25]

Characteristics and Features of the Substrate and Inocula

The sewage sludge used as substrate (primary and secondary mixed sludge) was collected from the San Fernando-Cádiz municipal wastewater treatment plant (MWTP) located in the south of Spain. The main characteristics and composition of the raw sludge used in the experiments were (average values of three determinations with standard deviations): pH, 5.4±0.2, total solids (TS), 44.4±0.8 g Kg^{-1}, volatile solids (VS), 33.0±0.5 g Kg^{-1}.

The mixed anaerobic culture used as thermophilic inoculum of the batch reactors was obtained from a lab digester running at an SRT of 15 days. The main characteristics of this digested sludge are as follows: pH 7.3±0.1, 31.2±1.4 g Kg^{-1} of TS, and 21.5±0.7 g Kg^{-1} of VS.

The sludge used as inoculum during the second stage operating at mesophilic conditions was collected from the aforementioned MWTP. The composition of solids from this inoculum was: 26.3±1.0 g Kg^{-1} of TS and 15.4±0.4 g Kg^{-1} of VS, the pH was 7.5±0.1

Experimental Procedure

Table 1 describes the experimental protocol used in the batch anaerobic digestion assays with the four operated reactors. A constant inoculum concentration (15 g VS L^{-1}) was used.

Three digesters (R1, R2 and R3) were filled with a mixture of thermophilic and raw sludges, with an inoculum substrate ratio (ISR), in terms of VS, corresponding to a value of 0.6.

The biogas production due to biomass decay and the possible presence of residual substrate in the inoculum was subtracted by performing a blank control. Therefore, in addition, a fourth reactor was inoculated, as a process control, without substrate. A 10 % v/v basal medium with macro and micronutrients was used; the composition of this solution has been described in detail by Raposo et al. [26]. The reactors were filled and flushed with an N_2 atmosphere in order to maintain anaerobic conditions before the experiments began.

After the thermophilic stage, all digesters were re-started up and inoculated with digested mesophilic sludge from the aforementioned MWTP. The thermostatic bath temperature was altered to 35ºC. The substrate in this case was the product of the thermophilic stage. The ISR of this phase was 2. The system remained under mesophilic conditions until the biodegradation process was completed, i.e. until no further methane production could be detected which were 15 days. All the experiments were carried out by triplicate. The experimental results shown in Figures were average values, the standard deviation of the mean values were lower than 5% in all cases.

Sampling and Analysis. Experimental Methods

Raw sludge and inocula as well as the influent and effluent of every stage of every test carried out were characterised according to the Standard Methods, [27] through: total and volatile solids, which were measured gravimetrically (2540B and 2540E, respectively). The pH was measured using a pH-meter model Crison 20 Basic and total alkalinity was measured by pH titration to 4.3.

Assay bottles were periodically analyzed for both quantitative and qualitative determination of biogas production. Quantitative biogas production was measured using a high precision flow gas meter – WET DRUM TG 0.1 (mbar) – Ritter – through a Tedlar bag, used as a gas sampling bag. Qualitative characterization (methane and carbon dioxide) of biogas was performed by a gas chromatograph SHIMADZU GC-14 B. The analysis method is given in detail elsewhere. [25]

The concentration and composition of VFA were analysed with a SHIMADZU GC-17A gas chromatograph equipped with a flame-ionisation detector and a capillary column filled with Nukol (polyethylene glycol modified by nitroterephthalic acid) as described by Riau et al. [25]

RESULTS AND DISCUSSION

Operational Performance

It was reported previously [25] that the VS reduction achieved in reactors R2 and R3 (experiments 2 and 3) were 45% and 52%, respectively, while in reactor R1 (experiment 1), only 37.5 % VS was removed. Therefore, the longer the retention time in the thermophilic digester, the greater the VS reduction.

Thermophilic conditions produced an effluent with elevated propionate concentrations (500–600 mg L^{-1}). Indeed, for the three experiments developed the mean total VFA concentration was also high, 981±43 mg acetic acid L^{-1}. Fortunately, the second-stage digesters reduced the amount of VFAs produced in the thermophilic reactors to concentrations of values lower than 10 mg acetic acid L^{-1}, meaning a reduction in the total volatile acidity of more than 95% in 15 days. Taking the destruction of VS into account, this means that the TPAD process can be considered as a stable and strong process for treating raw sludge, especially for thermophilic stage longer than 2 days. [25]

Kinetic Modelling

In order to kinetically characterize the two steps (thermophilic and mesophilic) of the temperature-phased anaerobic digestion process of sewage sludge, an analytical relationship was obtained between the volume of methane (reaction product) generated and the digestion time.

The Monod equation is normally used to correlate the growth rate of the microorganisms with the substrate concentration, S (g COD/L):

$$\frac{dX}{dt} = \frac{\mu_m \cdot S \cdot X}{(K_S + S)} \qquad (1)$$

where μ_m is the maximum specific growth rate, X is the microorganism concentration (g of volatile suspended solids, VSS/L) and K_S is the substrate affinity constant or saturation constant (g COD/L).

The yield coefficient of the microorganisms can be defined as:

$$Y_{X/S} = -dX/dS \qquad (2)$$

and hence:

$$dX/dt = Y_{X/S} \cdot (-dS/dt) \qquad (3)$$

By combining equations (1) and (3) the result is:

$$\frac{-dS}{dt} = \frac{k_I \cdot S \cdot X}{(K_S + S)} \qquad (4)$$

where k_I is an apparent kinetic constant defined as: $k_I = \mu_m / Y_{X/S}$

Because of the low cellular yield coefficient ($Y_{X/S}$) in anaerobic processes, [28-30] and taking into account that COD varied very little throughout the whole experiment, X can be assumed to remain fairly constant. Taking this into consideration, equation (4) can be converted into:

$$\frac{-dS}{dt} = \frac{k_2 \cdot S}{(K_S + S)} \qquad (5)$$

where k_2 is another apparent kinetic constant defined as: $k_2 = k_1 \cdot X$

From equation (5) two limit equations can be obtained:

Case a) for high substrate concentrations, where it is assumed that $K_S << S$ and equation (5) can be transformed into:

$$(-dS/dt) = k_2 \qquad (6)$$

Integration of equation (6) on the assumption that at $t = 0$, $S = S_0$ yields:

$$(S_0 - S) = k_2 \cdot t \qquad (7)$$

where S_0 is the initial substrate concentration.

The methane yield coefficient, $Y_{G/S}$ is defined by Borja et al., [30]:

$$Y_{G/S} = -dG/dS \qquad (8)$$

where G is the volume of methane gas accumulated after a given time t.

Integration of which when $G = 0$ for $S = S_0$ yields:

$$G = Y_{G/S} \cdot (S_0 - S) \qquad (9)$$

By combining equations (7) and (9), the result is:

$$G = k_3 \cdot t \qquad (10)$$

where k_3 is an apparent kinetic constant defined as: $k_3 = k_2 \cdot Y_{G/S}$

Equation (10) shows that as the volume of methane accumulated, methane production increased linearly with digestion time and represented a kinetic equation of zero order.

Case b) for low substrate concentrations, where it is assumed that $S << K_S$ and, therefore, equation (5) can be transformed into:

$$(-dS/dt) = k_4 \cdot S \qquad (11)$$

where k_4 is another apparent kinetic constant defined as: $k_4 = k_2/K_S$

By separating variables and integrating equation (11), taking into account again that at $t = 0$, $S = S_0$, the result is:

$$S_0/S = \exp(k_4 \cdot t) \qquad (12)$$

Considering the definition of the methane yield coefficient, $Y_{G/S}$, (equation (8) and the equation (9)), an integration of equation (12) gives:

$$G = G_m[1 - \exp(-k_4 \cdot t)] \qquad (13)$$

where G_m is the maximum volume of methane gas accumulated at an infinite digestion time.

Therefore, according to equation (13), methane production conforms to a first-order kinetic model for these conditions (low substrate concentrations). [31]

Figure 1 shows the variation of the volume of methane accumulated with digestion time for the thermophilic phase after 2 days (Reactor R1), 4 days (Reactor R2) and 6 days of digestion (reactor R3). These data corresponded to the values obtained for experiments 1, 2 and 3, respectively. As can be seen for the thermophilic phase the volume of methane accumulated increased linearly with the digestion time following a zero-order kinetics according to equation (10). The kinetic parameter, k_3, was calculated by linear regression and its value was 0.36 L CH_4 d^{-1}. In addition, the intercept of this linear fit was practically zero ($2.2 \cdot 10^{-16}$), which demonstrated how well the experimental data fits to the zerot-order kinetics.

The value of the kinetic constant of the thermophilic phase obtained in the present work was lower than that achieved in the thermophilic stages of temperature phased anaerobic digestion of other substrates such as a mixture of food wastes and flour (0.9 $days^{-1}$) [19] and medicine wastewater (0.75 $days^{-1}$). [20]

Figures 2, 3 and 4 show the variation of the volume of methane accumulated with time for the mesophilic phase after 2, 4 and 6 days of previous thermophilic digestion, respectively. As can be seen for the three cases studied and according to Equation 13, methane production conforms to a first-order kinetic model as predicted. This equation, which was obtained for lower substrate concentrations as occurred in the mesophilic step of this TPAD process once an important fraction of the initial substrate, has been degraded in the thermophilic phase. To be specific, figures 2-4 show curves whose shape coincides with that predicted by Equation 13. Thus, G was zero at $t = 0$, and the rate of gas production became zero at $t = \infty$. Hence, for the three mesophilic phases considered the experimental data fit to a first-order kinetic model.

Parameters G_m and k_4 were calculated from the experimental data (G, t) by using a non-linear regression program included in the SigmaPlot 11.0 software. Table 2 shows the G_m and k_4 values obtained with their corresponding standard deviations. Table 3 summarizes the most significant statistical parameters (such as the non-linear regression coefficient (R), coefficient of determination (R^2), standard error of estimate, normality test (Shapiro-Wilk), W statistic and significance level. The high values obtained for R

and R^2 and the low values of the standard errors of estimates for the three cases studied, especially for experiments 1 and 2 demonstrated the suitability of the proposed model for the mesophilic stages.

As can be seen in Table 2, the kinetic constant for the mesophilic phase was virtually identical for the three assays considered (0.21, 0.21 and 0.22 $days^{-1}$ for experiments 1, 2 and 3 respectively). This demonstrated that independently of the digestion time used in the thermophilic stage (2, 4 or 6 days, respectively) the kinetics of the second mesophilic phase was not affected.

On the other hand, the average value of the kinetic constant obtained in the mesophilic phase of the TPAD (0.21 $days^{-1}$) of raw sewage sludge from a MWTP is somewhat lower than that achieved in the mesophilic step of a TPAD process of a mixture of food waste and flour (0.4 $days^{-1}$) [19] and of the same order of magnitude as that obtained in the one-stage mesophilic anaerobic digestion of complex wastewaters such as wine distillery wastewaters and olive mill effluents. [30,32]

Figure 5 illustrates the methane production (L) per g of VS added as a function of time for the three experiments carried out, which was then corrected taking into account the control production and expressed at standard temperature and pressure (STP) conditions. As can be seen the methane yield was virtually proportional to the time applied during the thermophilic phase. Therefore, the ultimate methane yields were 0.067, 0.132 and 0.193 L CH_4 STP/g VS_{added} for experiments 1, 2 and 3, respectively. So, the methane yield increased 2.9 times when the thermophilic phase time increased by 3 (from 2 days in experiment 1 to 6 days in experiment 3).

The methane yield coefficient obtained in the TPAD of the raw sewage sludge after 6 days of the thermophilic period (0.193 L CH_4 STP/g VS_{added}) was somewhat lower than that obtained in the anaerobic codigestion of sewage sludge and food waste using the TPAD process (0.28 L CH_4 STP/g VS_{added}). [33]

CONCLUSIONS

A comprehensive kinetic model to correlate methane production with time was developed to describe the temperature phased batch anaerobic digestion of raw sludge derived from a municipal wastewater treatment plant.

It was found that the thermophilic phase of the TPAD process, carried out with 2, 4 and 6 days of digestion time followed a zero-order kinetics, the kinetic parameter of this step being 0.36 L CH_4 d^{-1}. By contrast, the mesophilic step of the process was described by a first-order model. The kinetic constant of this stage (0.21 $days^{-1}$) was virtually independent on the digestion time used in the thermophilic step.

Finally, the methane yield coefficient, $Y_{G/S}$, was practically proportional to the time applied during the thermophilic stage. This value was equal to 0.067, 0.132 and 0.193 L CH_4 STP/g VS_{added} for experiments 1, 2 and 3, respectively.

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FIGURE CAPTIONS

Figure 1. Variation of the volume of methane gas accumulated with digestion time for the three experiments carried out during the thermophilic stage and linear regression of the adjustment of the experimental data to a zero-order kinetic equation.

Figure 2. Variation of the volume of methane gas accumulated with digestion time for experiment 1 carried out during the mesophilic stage and non-linear regression of the adjustment of the experimental data to a first-order kinetic equation.

Figure 3. Variation of the volume of methane gas accumulated with digestion time for experiment 2 carried out during the mesophilic stage and non-linear regression of the adjustment of the experimental data to a first-order kinetic equation.

Figure 4. Variation of the volume of methane gas accumulated with digestion time for experiment 3 carried out during the mesophilic stage and non-linear regression of the adjustment of the experimental data to a first-order kinetic equation.

Figure 5. Variation of the methane yield with time for the three experiments carried out.

Figure1

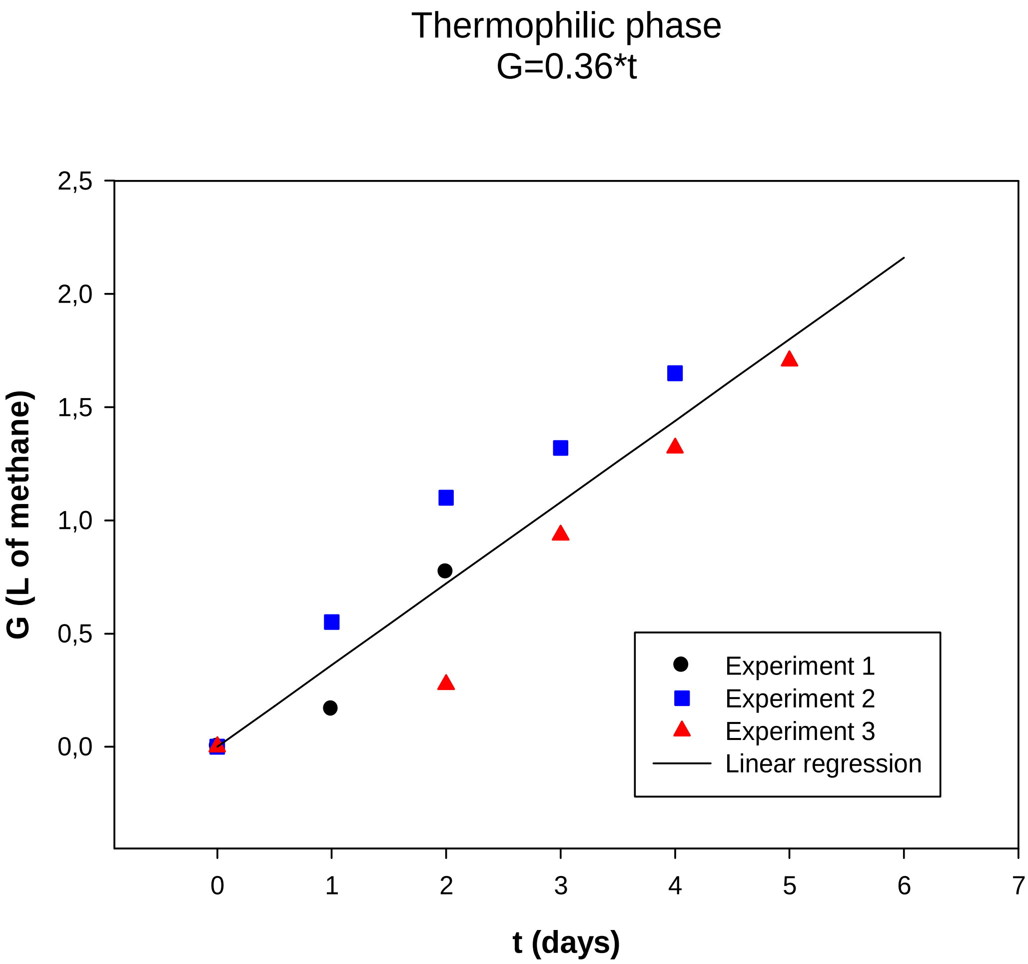

Thermophilic phase
G=0.36*t
G (L of methane)
2,5
2,0
1,5
1,0
0,5
0,0
0
1
2
3
4
5
6
7
t (days)
Experiment 1
Experiment 2
Experiment 3
Linear regression

Figure 2

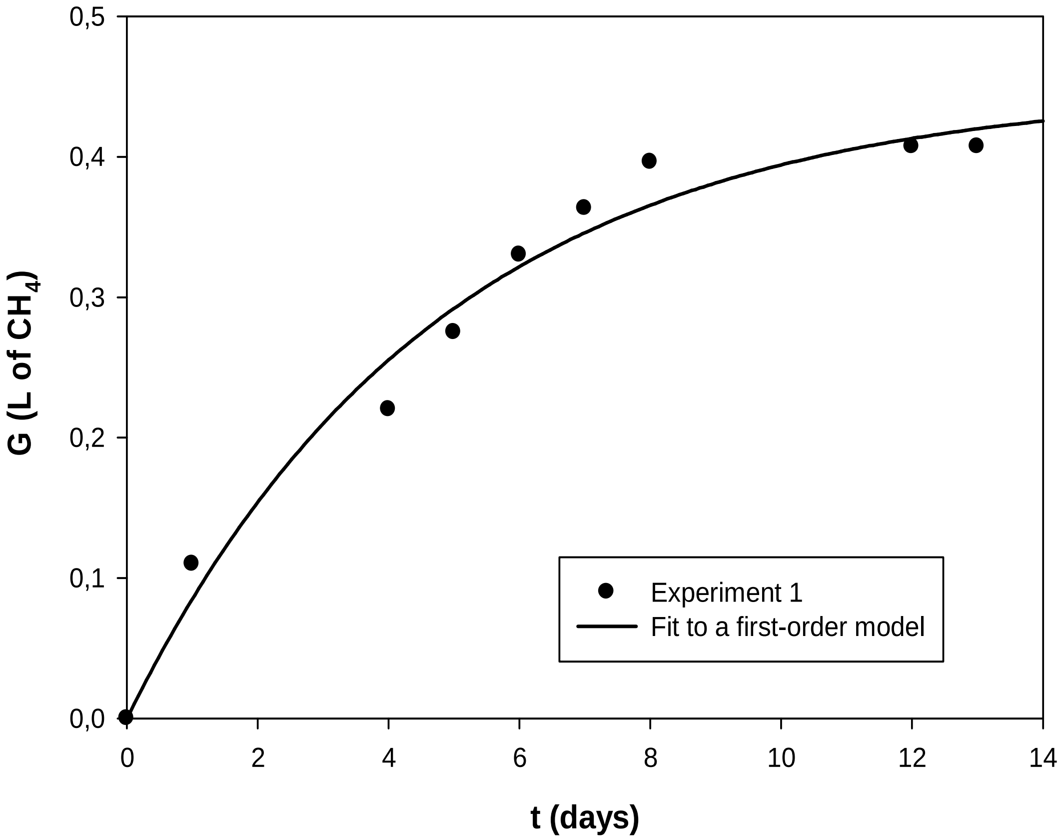
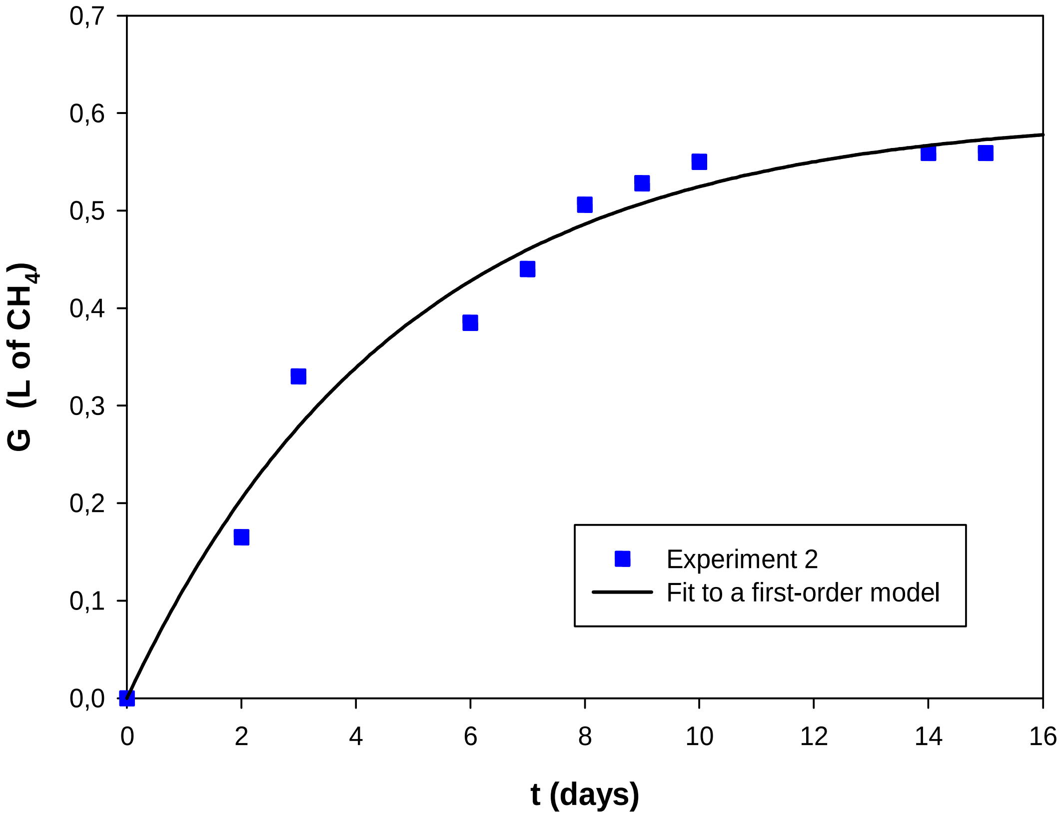
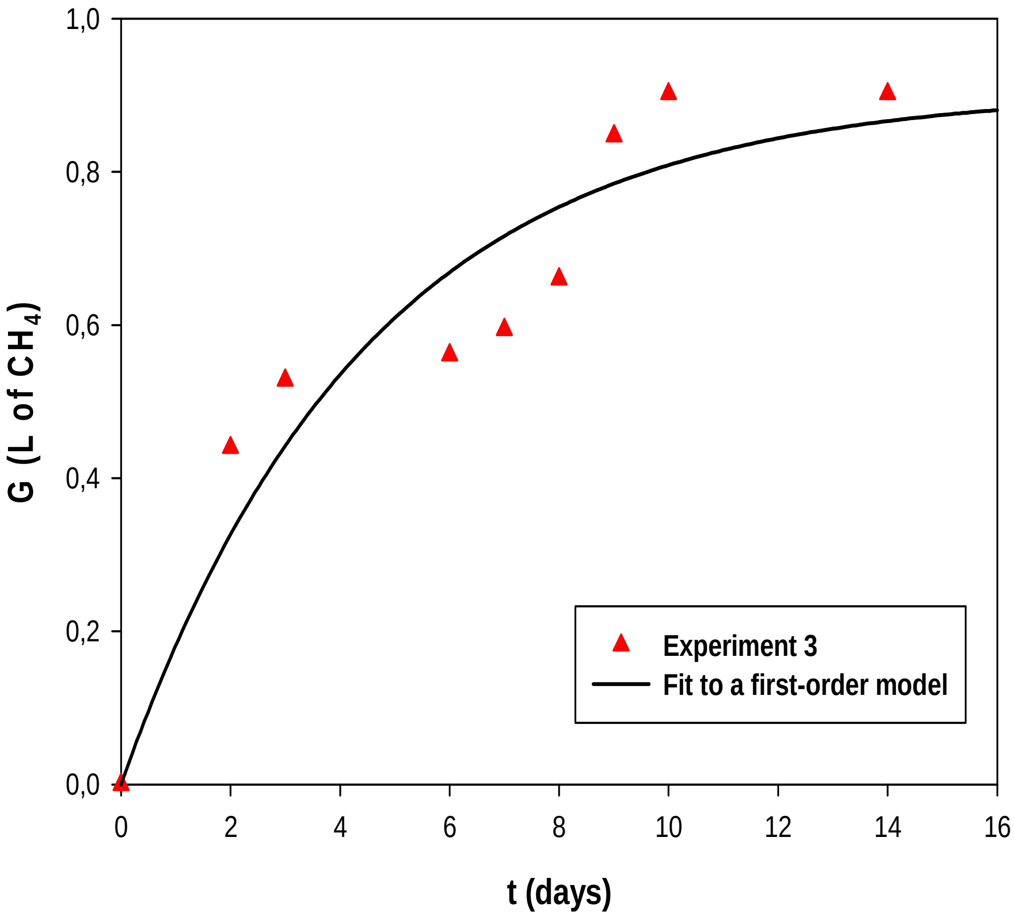

G (L of CH_4)
0,0
0,1
0,2
0,3
0,4
0,5
0
2
4
6
8
10
12
14
t (days)
Experiment 1
Fit to a first-order model

Figure 3



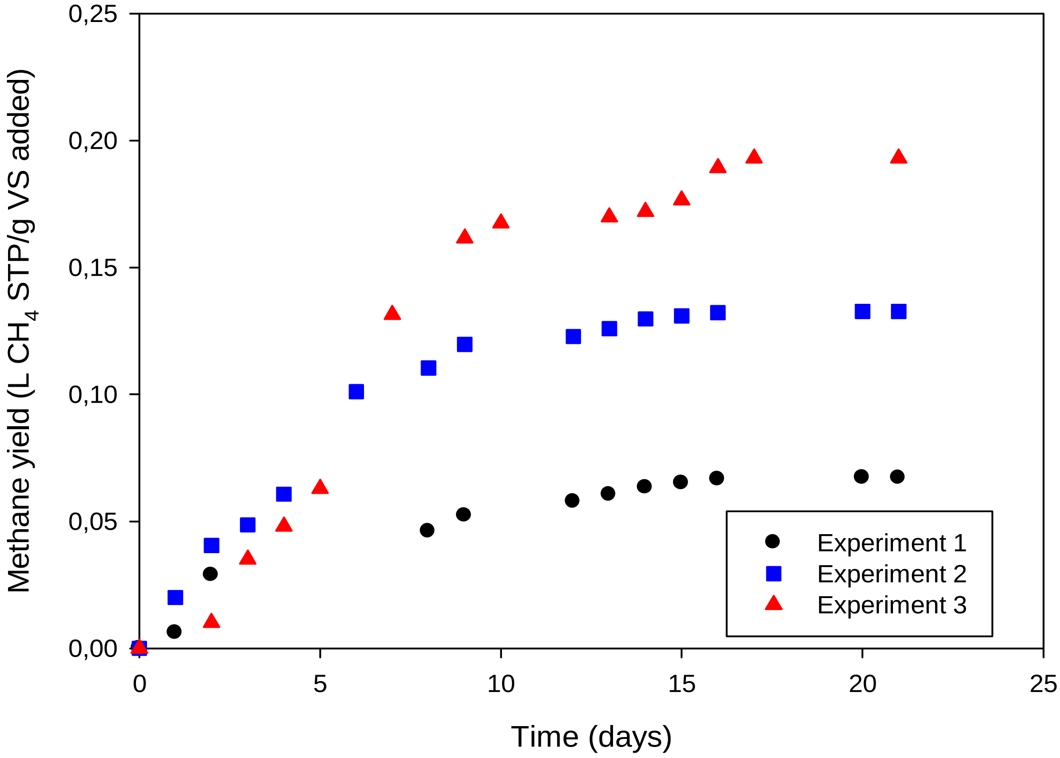
G (L of CH4)
0,0
0,1
0,2
0,3
0,4
0,5
0,6
0,7
0
2
4
6
8
10
12
14
16
t (days)
Experiment 2
Fit to a first-order model

Figure 4



1,0
0,8
0,6
0,4
0,2
0,0
G (L of CH4)
0
2
4
6
8
10
12
14
16
t (days)
Experiment 3
Fit to a first-order model

Figure 5



0,25
0,20
0,15
0,10
0,05
0,00
Methane yield (L CH4 STP/g VS added)
0
5
10
15
20
25
Time (days)
Experiment 1
Experiment 2
Experiment 3

Table 1. Time elapsed under thermophilic and mesophilic phases for the experiments carried out

Experiment	Thermophilic phase	Mesophilic phase
	Time (days)	
1	2	15
2	4	15
3	6	15
Blank control	6	15

Table 2. Values of the kinetic parameters, G_m and k_4, obtained for the mesophilic phase of the TPAD process for the three experiments carried out.

Parameter	Experiment 1	Experiment 2	Experiment 3
G_m (L CH_4)	0.45 ± 0.02	0.60 ± 0.03	0.91 ± 0.09
k_4 ($days^{-1}$)	0.21 ±0.03	0.21 ± 0.03	0.22 ± 0.06

Table 3. Statistical parameters obtained in the adjustment of the experimental data of the mesophilic phase to the first-order kinetic model (equation (13) for the three cases studied.

Parameter	**Experiment 1**	**Experiment 2**	**Experiment 3**
Non-linear regression coefficient (*R*)	0.989	0.987	0.964
Coefficient of determination (R^2)	0.978	0.975	0.956
Standard error of Estimate	0.022	0.031	0.079
Normality test (Shapiro-Wilk)	Passed (P = 0.948)	Passed (P = 0.813)	Passed (P = 0.534)
W statistic	0.977	0.962	0.917
Significance level	0.05	0.05	0.05