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Application of simplified models for anaerobic biodegradability tests. Evaluation of pre-treatment processes

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ABSTRACT

The effect of thermal and sonication pre-treatment on the anaerobic degradation of sewage sludge was evaluated through the calculation of performance parameters by using three simplified mathematical models and one kinetic model. The Modified Gompertz equation, the Logistic function, Reaction Curve and First-Order models were all used with experimental data from the anaerobic biodegradability tests fed with primary and secondary thermal pre-treated sludge, and secondary sonicated sludge. All the models fit well with the experimental data, but the Reaction Curve model presented the best agreement in the fitting process. From the first-order equation no significant changes were observed in the hydrolysis constant under all conditions. Thermal pre-treatment (175 °C and 30 min) showed an important effect on the secondary sludge reaching an improvement of around 90% and 80% in the maximum production rate and the total biogas produced respectively. With regards to the sonication experiment, the best result was obtained when 12,400 kJ/kgTS were used, reaching an improvement of 40% in the total biogas production.

1. Introduction

Due to environmental, economic, social and legal factors, the treatment and disposal of excess sludge represent a bottleneck for wastewater treatment plants. An overview on the state-of- the art shows that there are three different strategies: (i) reduce aerobic sludge production by introducing additional steps to lower the cellular yield coefficient, (ii) sludge pre-treatment before anaerobic digestion, (iii) sludge elimination [1]. Although anaerobic digestion is widely used to stabilize sludge, pre-treatment technologies are gaining acceptance. The overall anaerobic degradation of sewage sludge is generally limited by the hydrolysis rate of organic suspended matter [2,3]. By improving the hydrolysis step, solid substrates are more accessible to anaerobic bacteria, accelerating the digestion, increasing the volume of biogas produced and decreasing the amount of sludge to be disposed of. The main physical pre-treatments founded at research or commercial levels are: microwave irradiation [4], Ultrasonic homogenizers [5,6] and thermal hydrolysis [7,8].

Most of the studies about pre-treatment methods evaluate the efficiency of the process comparing COD solubilisation and the total biogas produced with a control experiment (untreated sludge) [7–9]. However, from a practical point of view, the goal of the pre-treatments is to increase the productivity and the total biogas production. In most of the research studies in this field, the only parameter considered is the final quantity of biogas produced and not the biogas production rate. Chu et al. [10] determined the methane production rate, but it was not informed how this was done. Therefore, the establishment of methodologies to evaluate the effectiveness of each pre-treatment becomes necessary.

Few studies have applied mathematical models in the anaerobic degradation of pre-treated sludge in order to obtain some kinetic parameters. Tomei et al. [11] used several kinetic models, but focused only in the hydrolysis reaction to evaluate the F/I (substrate/inoculum) ratio in sonicated sludge. Other models have been implemented for the solubilisation of COD in the pre-treatment processes, but not on the anaerobic digestion of pre-treated sludge [9,12].

The aim of this study is the application of three practical mathematical models and one kinetic model in conventional biodegradability anaerobic testing. This model evaluation was carried out using experimental data obtained from two different lab-scale experiments of thermal and sonicated pre-treated sewage sludge.

2. Material and methods

2.1. Thermal pre-treatment

In this experiment primary and secondary sludge from conventional municipal WWTP1 was used. The system for thermal pre-treatment, consisted of a feeding tank, a progressive cavity pump (P_{max} = 12 bar), a steam boiler, a 20 L total volume hydrolysis reactor (V_{utile} = 10 L) connected to a flash tank (V = 100 L) with outlet pipes for steam and hydrolyzed sludge. The pilot plant is

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Nomenclature

SSwP	secondary sludge without pre-treatment
PSwP	primary sludge without pre-treatment
SSThP	secondary sludge thermal pre-treated
PSThP	primary sludge thermal pre-treated
WWTP	wastewater treatment plant
COD	chemical oxygen demand
Es	specific energy applied
P	ultrasonic power
t	time of application
V	volume sample
TSo	initial total solid concentration
F/I	feeding/inoculum ratio
LM	logistic modified
GM	Gompertz modified
RC	reaction curve
FO	first order
B	biogas produced
P	maximum biogas production
Rm	maximum biogas production rate
Λ	lag time
B_0	degradation extent
k_h	apparent hydrolysis rate coefficient

equipped with automatic valves that control the steam entrance from the boiler and the sludge exit from the reactor to the flash. A data acquisition and control system is used to measure pressure and temperature and automatically controls the steam inlet and the hydrolyzed sludge exit to the flash. The pump introduces 10 L of sludge into the reactor, and then the steam valve is opened until pressure and temperature reach the reference level. At the end of the reaction time the decompression valve is automatically opened and the hydrolyzed sludge flows to the flash tank. In agreement with previous experiences made in a pilot-laboratory equipment (V = 1 L), the reaction time maintained for all the experiments was 30 min at 175 °C temperature. This pre-treatment was applied on primary and secondary sludge.

2.2. Ultrasound pre-treatment

In this experiment secondary sludge from conventional municipal WWTP2 was used. The ultrasound apparatus used was a continuous ultrasonic homogenizer, Hielscher model UP400S. The equipment consists of a flow cell with a volume of 15 mL, equipped with a sonotrode (frequency 24 kHz and maximal theoretical power 400 W), refrigerated with water. Sludge is continuously pumped through the cell (V = 15 mL), and the desired Es is determined according to Eq. (1):

$$Es = \frac{P \cdot t}{V \cdot TSo} \tag{1}$$

Table 1 presents the sonication conditions of secondary sludge. Table 2 presents the concentration of VS for all the experimental conditions prior and after each pre-treatment.

Table 1
Sonication conditions for the batch biodegradability study.

		S0A	S0A1	S0A2	S0A3	S0A4
Power		100 W				
Sonication time	s	0	2	6	12	60
Energy applied	J/mL	0	13	40	80	360
	kJ/kg DS	0	460	1377	2754	12,400

Table 2
Concentration of VS (g/L) of raw and pre-treated sewage sludge.

	Thermal pre-treatment				
WWTP 1	PSwP 93.7	PSThP 23.6	SSwP 37.90	SSThP 18.3	
	Sonicated pre-treatment				
WWTP 2	S0A 21.8	S0A1 21.1	S0A2 20.3	S0A3 21.1	S0A4 18.9

2.3. Anaerobic biodegradability tests

Batch experiments were run in glass serum bottles with a liquid volume of 120 mL (60 mL of total volume). All the experiments were carried out at 35 ± 0.6 °C in a thermostatic room. Biogas production was measured manually by a pressure transmitter (Druck, PTX 1400, range 1 bar). Sludge from a pilot-scale anaerobic digester treating mixed waste-activated sludge, with a concentration of 13.7 gVS/L was used as inoculum for the anaerobic test. Solid concentrations were estimated by heating (105 °C during 24 h for total solids and 550 °C during 2 h for mineral solids concentration). Volatile solid concentrations were deduced. Serum bottles of 60 mL of volume and an F/I ratio of 0.5 gVS/gVS was used for all the experiments. Anaerobic biodegradability was calculated following Biogas production was measured manually by a pressure transmitter (Druck, PTX 1400, range 1 bar) in the head space of each reactor. After the daily pressure measurement, the biogas in the head space was released, what reduced the pressure in the head space to atmospheric pressure. These pressure differences were converted to into biogas volume, using the ideal gas Law and standard conditions (P = 1 bar and T = 0 °C).

2.4. Models for data fit

Three models to estimate performance parameters and one model to estimate kinetic parameters were used. The *Modified Gompertz equation* (*GM*) (Eq. (2)) which has been used, initially, for methane production [13] and, more frequently, for hydrogen production [14–16]:

$$B = P\,\exp\left(-\exp\left(\frac{Rm \cdot e}{P}(\lambda - t) + 1\right)\right) \tag{2}$$

The *Logistic function* (*LM*) fits the global shape of the biogas production kinetics: an initial exponential increase and a final stabilization at a maximal production level. This model assumes that the rate of gas production is proportional to the amount of gas already produced, the maximum production rate and the maximum capacity of biogas production. This model has been used for anaerobic fermentation, as well as, for estimate the methane production in landfill leachate [17,18]. In this case a modified version of the logistic function was used (Eq. (3)) [19]:

$$B = \frac{P}{1 + \exp(4Rm(\lambda - t)/P + 2)} \tag{3}$$

The *transference function* (*Reaction curve-type model*) (*RC*), used mainly for control purposes, which considers that any process might be analyzed as a system receiving inputs and generating outputs, was also evaluated (Eq. (4)). This type of model has been implemented in anaerobic digestion in some cases [20]:

$$B = P\left(1 - \exp\left(-\frac{Rm(t - \lambda)}{P}\right)\right) \tag{4}$$

Finally, the maximum biogas yield or degradation extent (B_0) and the apparent hydrolysis rate coefficient (k_h) were obtained using the first-order equation (FO) (Eq. (5)) [21]. This turns into a crucial kinetic parameter in the case of anaerobic degradation of solid waste (as waste-activated sludge), where the hydrolysis reaction becomes the limiting reaction that governs the overall process [3]:

$$B = B_0(1 - \exp(-k_h \cdot t)) \quad (5)$$

Nonlinear optimization (using Matlab® 7.0) by least squares procedure is applied to calculate the unknown parameters by minimizing a cost function (Eq. (6)), which measures the difference between the experimental measurements and the corresponding simulated value (the values obtained with the linearization method are used as initial values in the simulation process).

$$J(\psi) = \min \sum_{t=1}^{N} (\eta_m(t) - \eta(t, \psi))^2 \quad (6)$$

where J is the objective function, η_m is the consumption velocity obtained from measurements, η is the corresponding simulated velocity and N is the number of measurements. The optimization

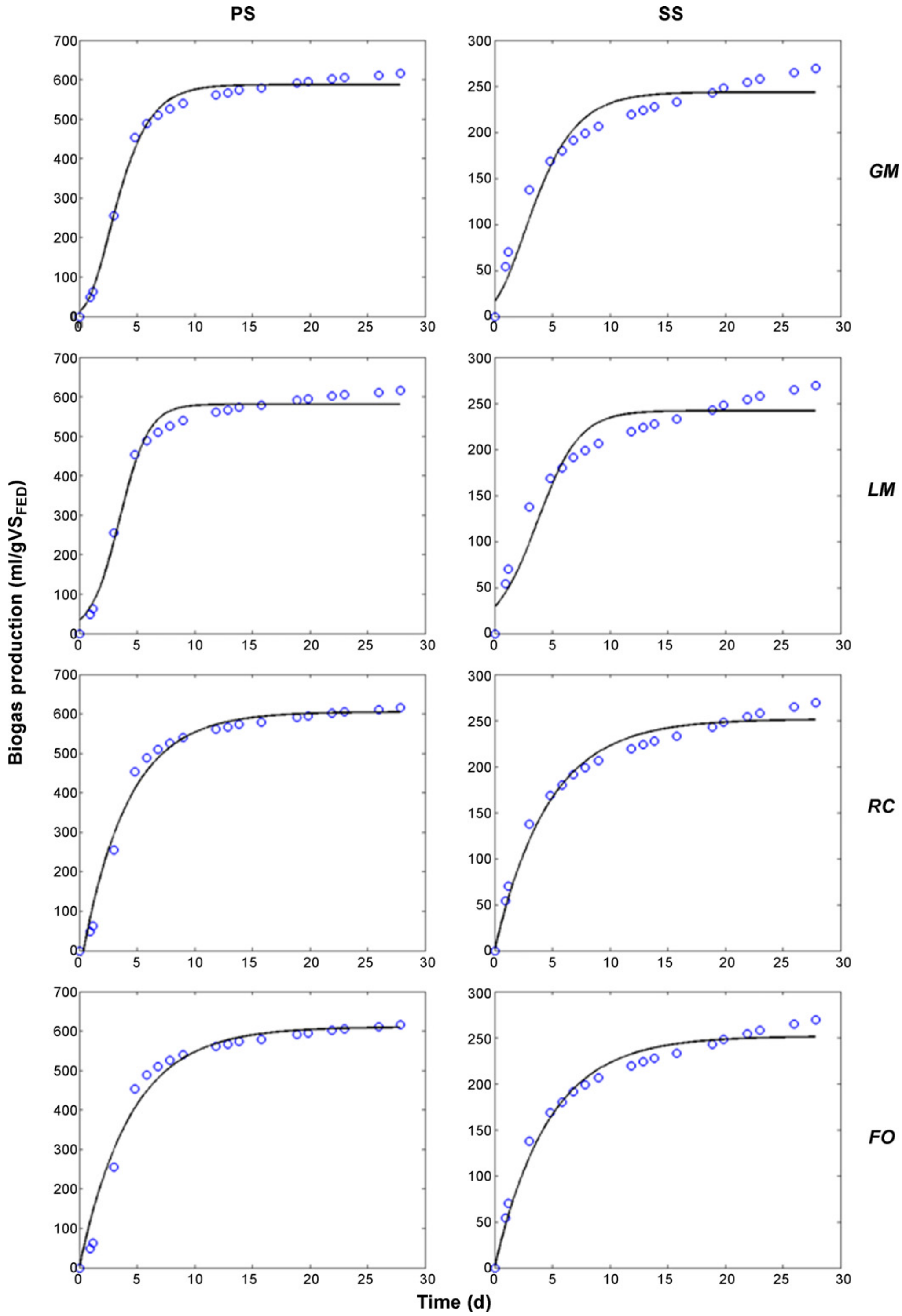

Fig. 1. Models fit with biogas production of anaerobic test using raw sludge (without pre-treatment) as substrate.

process ended when the change in the residual was less than the specified tolerance set on 1e-7.

3. Results and discussion

3.1. Thermal pre-treatment

Figs. 1 and 2 show the model fit (solid line) with the experimental data for both primary and secondary raw and pre-treated sludge from each assay (circles). Table 3 presents the parameters obtained in the optimization process and demonstrates the adequate fit of each case. All models were fit with experimental data from anaerobic biodegradability tests.

In general, there was an overall agreement between all the models and the experimental data. Comparing the performance models (*GM*, *LM* and *RC*) the best fit was obtained using the *Reaction Curve* model which reached the highest regression of coefficients in all cases (above 0.97), which means that this model might explain the 97% (and over) of total variation in the data. Likewise, the *SSEe* that

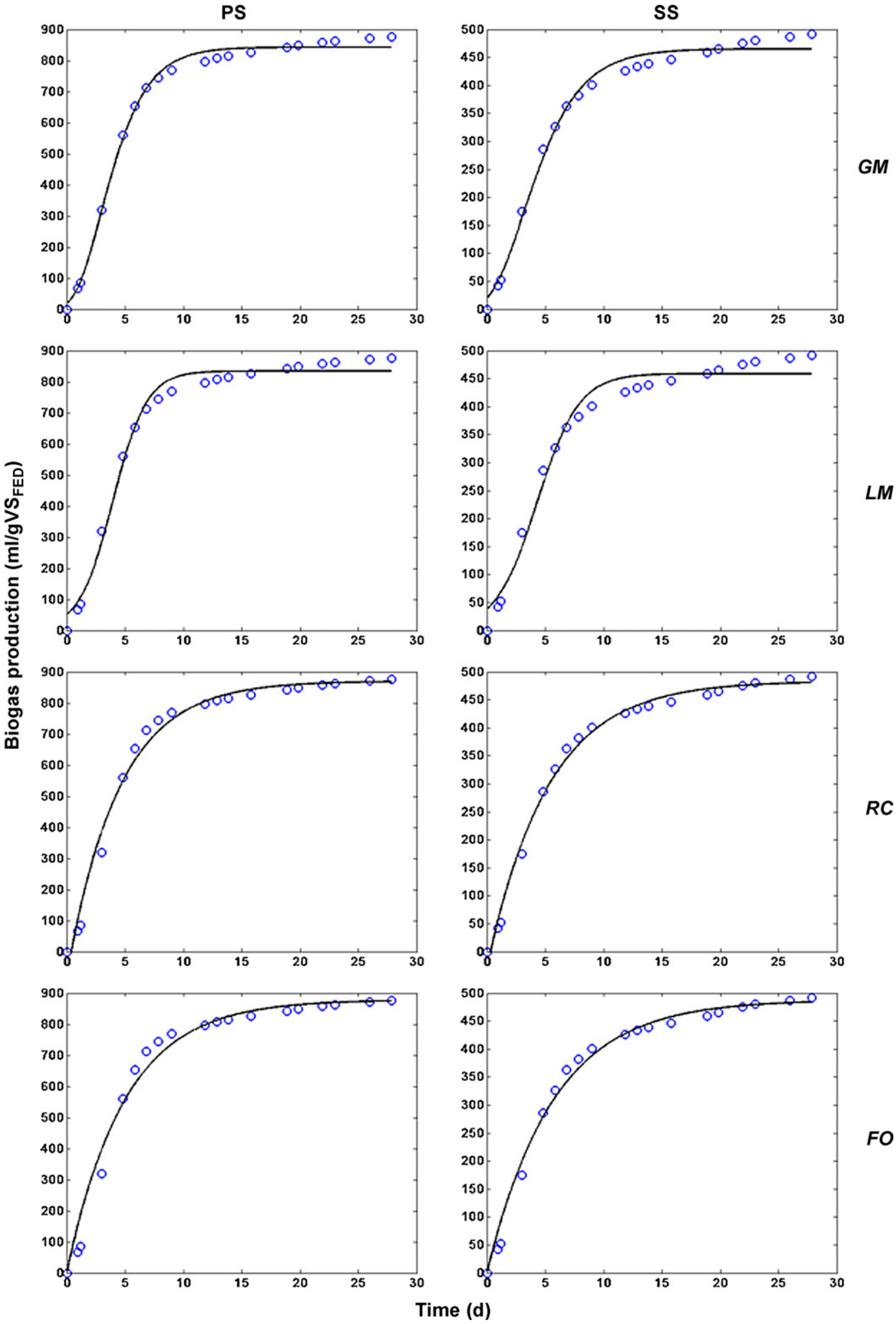

Fig. 2. Models fit with biogas production of anaerobic test using thermal pre-treated sludge as substrate.

Table 3
Parameters and goodness fit obtained with the evaluated models.

	Primary				Secondary			
	GM	*LM*	*RC*	*FO*	*GM*	*LM*	*RC*	*FO*
Raw sewage sludge								
P (ml/gVS)	587.3	581.1	605.3	610.3	243.5	241.9	251.5	251.5
Rm (ml/gVS d)	112.3	115.8	153.9	–	35.5	32.9	54.4	–
k_h (d^{-1})	–	–	–	0.23	–	–	–	0.22
λ (d)	0.71	1.00	0.37	–	0	0	0	–
R-square	0.993	0.986	0.983	0.975	0.949	0.935	0.982	0.982
SSEe[a]	15.61	16.31	13.69	12.43	15.92	15.70	15.00	15.00
Pre-treated sewage sludge								
P (ml/gVS)	842.9	834.3	870.3	878.3	465.3	458.9	483.4	487.8
Rm (ml/gVS d)	140.8	143.9	196.6	-	62.9	64.1	92.8	–
k_h (d^{-1})	–	–	–	0.20	–	–	–	0.18
λ (d)	0.75	1.06	0.39	–	0.41	0.72	0.31	–
R-square	0.996	0.990	0.986	0.979	0.992	0.980	0.993	0.990
SSEe[a]	15.20	16.14	13.52	12.20	16.00	16.09	15.27	13.26

[a] Sum of square due to error residuals standardized.

measures the total deviation of the response values from the fit to the response values was the lowest for the *RC* model, which made the fit more useful for prediction. Another important issue is the shape of the modeled curves. At $t = 0$, the biogas production is not null for *GM* and *LM* models, which has no physical meaning. In the case of *GM*, when λ is negligible and $t = 0$, *B* converge to *P*/(exp(exp)) which is a positive value, but when $\lambda > 0$ and $t = 0$, *B* converges to 0. This is why this equation is used mainly in hydrogen production where a significant lag time occurs because a specific population is used. Despite of this, in this case, the evaluation was focused mainly in the values of *Rm* and *P*, considering that in biogas production (methane), lag time is negligible. A similar situation is found for *LM*.

On the other hand, *GM* and *LM* show null biogas production at $t > 10$ d, which is slightly different when *RC* is used. In that period, slowly biodegradable compounds are degraded; hence the biogas production from these compounds would be more appropriately represented by *RC* model.

A comparison between three models was also done by Altas [19], who used Gompertz, Logistical and Richard equations fit with biogas production from anaerobic batch tests at different levels of metal concentrations. The correlation with the experimental data was only evaluated through the correlation coefficient which was over 0.99. Gompertz and Richard showed similar values of the parameters; nevertheless, Richard equation has one more parameter (*d*, shape coefficient of the curve) decreasing the degrees of freedom adjusted *R*-square.

With regards to the parameters determination, the main difference between the models was observed with the *Rm* value, where the *RC* model presented values up to 60% greater than those obtained with the other models. This can be explained because the *GM* and *LM* showed small deviations, mainly at the beginning of the experiment underestimating the maximum slope of the curve. The lag time (λ) was negligible in most of the cases, which indicates that the soluble material was quickly consumed by the anaerobic biomass. The value of *P* was estimated in a similar way for all models showing deviations around 6%.

In order to evaluate the effects of thermal pre-treatment on the biogas production (*P*) and on the maximum biogas production rate (*Rm*), the increase with respect to the corresponding untreated sludge was calculated using Eq. (7). The results obtained are presented in Fig. 3:

$$\%\text{Increase} = \frac{(P \text{ or } Rm)_{\text{pret}} - (P \text{ or } Rm)_{\text{wpret}}}{(P \text{ or } Rm)_{\text{wpret}}} \times 100 \quad (7)$$

It can be noted, from Fig. 3, that there was an increase in the maximum biogas production (*P*) using thermal pre-treated sludge. Comparing the sludge type, thermal pre-treatment had a major effect on the secondary sludge, reaching an increase close to the 90%. This was expected because the *SS* has a higher concentration of suspended solids than the primary one, thus, more soluble compounds are released after pre-treatment, which means that more readily soluble organic matter is available to be converted into methane. For the same reason, a significant increase in the maximum production rate (*Rm*) is observed, as more readily degraded organic matter is available. In the case of the *PS*, the solubilisation obtained with the thermal pre-treatment was less, and therefore, the increase in *P* and *Rm* was also less.

Similar results were obtained by Valo et al. [8] in biodegradability batch tests at the same temperature with 1 h of thermal pre-treatment, but no details on the type of sludge used were given. Bougrier et al. [9,22] reported increase in the biogas production under the same experimental conditions than in the present study. However, the increase in biogas achieved was higher (more that 100%) due to the fact that the control was poorly degradable (as the soluble COD of the fresh sludge was negligible). Less increases were obtained by Bougrier et al. [7] in a semi-continuous reactor fed with thermal pre-treated sludge at 135 °C and 190 °C.

First-order model agreed with the experimental data as it is shown in Figs. 1 and 2, in both, the curve shape and the goodness fit parameters. Regarding the degradation extent, an important difference is observed between primary and secondary sludge. The latter was expected, since primary sludge has a greater amount of readily degradable soluble compounds. This difference decreased in the case of pre-treated sludge, since more new soluble material was released in the pre-treatment of secondary sludge. The apparent hydrolysis rate coefficient (k_h) did not show representative variations between the sludges in neither prior or after pre-treatment. The values obtained in this study matched the literature values [3,21].

3.2. Sonication pre-treatment

Fig. 4 shows the model fit (solid line) with the experimental data from each assay (circles). Table 4 presents the parameters obtained in the fitting process.

As was obtained in the thermal pre-treatment case, there was a good agreement between all the models and the experimental data, but the best fit was obtained with *RC*, according to the determination coefficient and the *SSEe*. The curves shape show the same behavior as it was described for thermal pre-treatment.

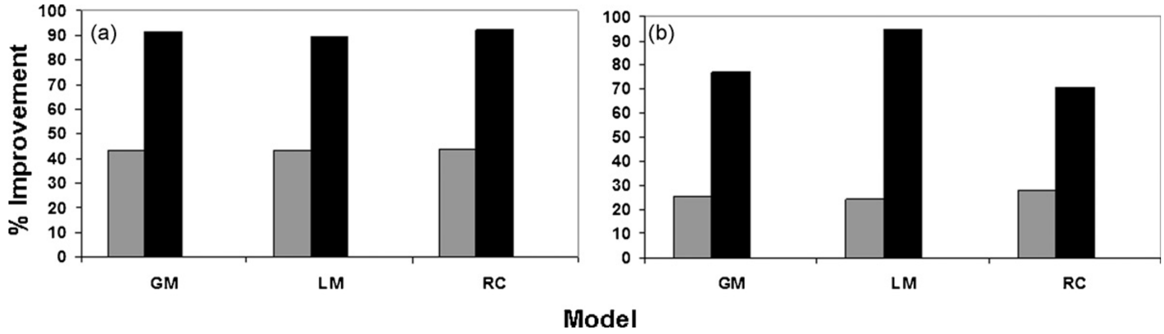

Fig. 3. (a) Increase of the biogas production (*P*) and (b) increase of the maximum biogas production rate (*Rm*) according to the models for each type of sludge used in the thermal pre-treatment experiment. Grey bar: primary sludge, Black bar: secondary sludge.

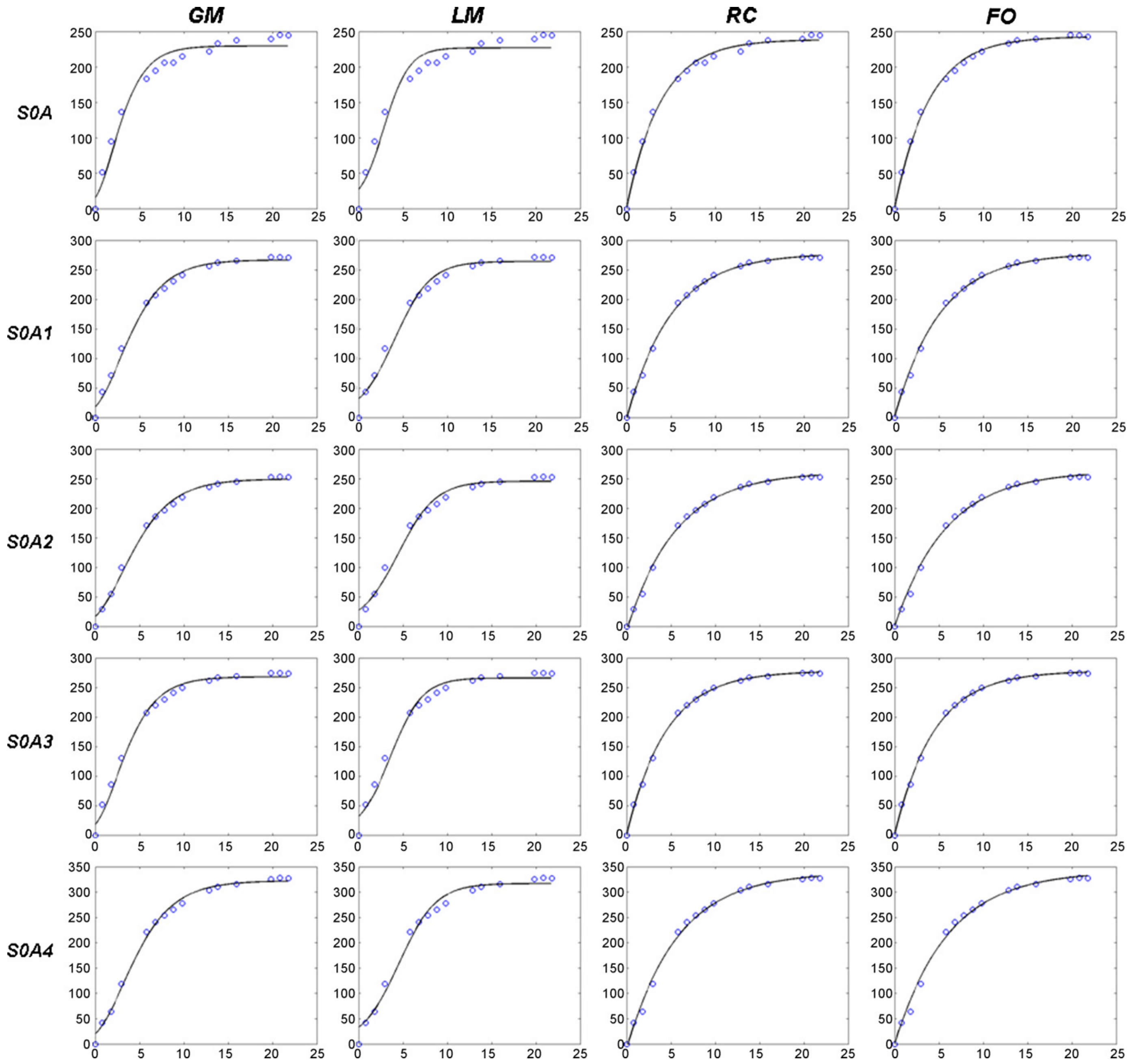

Fig. 4. Models fit with biogas production of anaerobic test using sonicated pre-treated sludge as substrate.

Table 4
Kinetic parameters calculated by the models for sonicated sewage sludge.

	GM	LM	RC	FO
S0A				
P (ml/gVS)	229.6	227.0	238.7	242.8
Rm (ml/gVS d)	42.09	39.88	62.31	–
k_h (d^{-1})	–	–	–	0.26
λ (d)	0	0	0	–
R-square	0.968	0.951	0.997	0.997
SSEe[1]	13.34	13.01	11.92	11.56
S0A1				
P (ml/gVS)	266.9	264.35	277.7	278.3
Rm (ml/gVS d)	35.40	32.68	55.44	–
k_h (d^{-1})	–	–	–	0.20
λ (d)	0	0	0.05	–
R-square	0.992	0.983	0.998	0.998
SSEe[1]	11.63	10.38	10.46	9.89
S0A2				
P (ml/gVS)	249.6	245.8	261.2	263.0
Rm (ml/gVS d)	29.92	29.00	47.19	–
k_h (d^{-1})	–	–	–	0.17
λ (d)	0	0.21	0.15	–
R-square	0.994	0.984	0.997	0.997
SSEe[1]	10.27	10.66	9.83	10.1
S0A3				
P (ml/gVS)	268.27	266.2	277.9	277.9
Rm (ml/gVS d)	40.51	37.11	62.90	–
k_h (d^{-1})	–	–	–	0.23
λ (d)	0	0	0	–
R-square	0.990	0.979	0.999	0.999
SSEe[1]	11.81	11.03	9.73	9.73
S0A4				
P (ml/gVS)	322.5	317.1	339.1	341.5
Rm (ml/gVS d)	38.58	37.88	59.49	–
k_h (d^{-1})	–	–	–	0.17
λ (d)	0.09	0.34	0.16	–
R-square	0.995	0.986	0.995	0.994
SSEe[1]	11.65	11.17	10.19	9.38

First-order model agreed with the experimental data as it is shown in both curve shape and goodness of fit, even better than with thermal pre-treatment. The degradation extent was increasing slightly as the sonication energy was increasing; however, the most significant rise was observed in S0A4 condition. The sonication energies applied did not have a clear effect on the apparent hydrolysis rate coefficient (k_h), but a small decreasing trend was observed as the energy increased. This coefficient is an apparent constant, and might be influenced by several factors as temperature, pH, and particulate organic properties. In this case, the environmental conditions were the same for all the experiments, hence the properties of the particulate organic matter that remained after each pre-treatment could have been changed, and also, the enzymatic hydrolysis process.

In regards to the pre-treatment effect, there was only a significant rise in the potential biogas production (*P*), as it shown in Fig. 5, whereas, the maximum biogas production rate (*Rm*), was not affected by the sonication pre-treatment. This situation could be due to the fact that sludge (from WWTP2) had already a significant amount of soluble organic matter, in the saturation part of the Monod Curve; thus, any increase of the concentration soluble organic matter was not going to affect the growth rate and, consequently, the biogas production rate, but the maximum biogas produced.

The greatest increase in the maximum biogas production was achieved under S0A4 condition (12,400 kJ/kg) whereas; small increases were achieved with the other conditions, which means that, under these experimental conditions, a specific energy of up to 2754 kJ/kg did not produce a significant effect on the particulate organic matter disintegration.

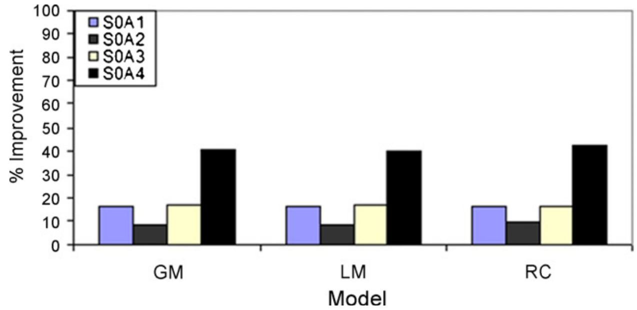

Fig. 5. Increase of the biogas production (*P*) according to the models for each type of WAS used in the sonication pre-treatment experiment.

The maximum biogas production achieved, under S0A4 condition, were higher than those obtained by Quarmby et al. [5], who improved the biogas production only a 13% with the same energy applied in the present study, and a 15%, when applying a 3-fold energy. A rise of 15% in the methane yield was also achieved by Forster et al. [23] using a similar specific energy than in S0A3 (1680 kJ/kg), obtaining an increase over 15%. Braguglia et al. [12] obtained a 25% increase in the biogas production in the range 4500–5000 kJ/kgTS. Bougrier et al. [22] evaluated two sonication energy levels (6250 and 9350 kJ/kg) reaching a 51% and 53% increase in the methane yield for each condition. These values are higher than those obtained in S0A4, probably due to the different TS concentrations of the sludge. The energy applied in this study is also in agreement with Bougrier et al. [24], who observed increase in biogas production between 1350 kJ/kgTS and 7000 kJ/kgTS. By contrast, Laffitte-Trouqué and Foster [25] did not find any positive effects with doses between 3400 and 5000 kJ/kg in a semi-continuous operation, both in mesophilic and thermophilic anaerobic degradation of the sonicated sludge. Quite a good improvement was obtained by Chu et al. [10] who reached a percentage of increase of 290% and 104% in the production rate and the methane yield, respectively. Nevertheless, these results were obtained by applying a higher sonication energy (42,000 kJ/kgTS), and using adapted anaerobic biomass.

4. Conclusions

The use of three simple models in the anaerobic degradation of untreated and pre-treated sewage sludge showed to be a proper tool used to obtain performance parameters, allowing for a more reliable comparison between the digestion of raw and pre-treated sludge. In spite of the proper results obtained, Modified Gompertz and Logistic models showed worse agreements with the experimental data than the Reaction curve model, which fit very well. Hence, by using this model, the maximum biogas production and the maximum biogas production rate can be calculated accurately for batch anaerobic digestion of sewage sludges. A first-order model can be used for the degradation extent determination which is related with maximum biogas production. Nevertheless, the hydrolysis constant did not show a clear trend after both pre-treatments, therefore it does not seem to be a good indicator of the pre-treatment effect. However, its value is important if more complex models are going to be used for predictions.

Thermal pre-treatment improved the anaerobic biodegradability of primary and secondary sludge, in both maximum biogas production rate and maximum biogas produced. Sonication pre-treatment, significantly enhanced, the total biogas produced only at 12,400 kJ/kg, but the maximum biogas production rate remained relatively constant.

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