



# From pre-treatment toward inter-treatment. Getting some clues from sewage sludge biomethanation



Eduardo Ortega-Martinez<sup>a</sup>, Ieva Sapkaite<sup>c</sup>, Fernando Fdz-Polanco<sup>c</sup>, Andres Donoso-Bravo<sup>a,b,\*</sup>

<sup>a</sup> Escuela de Ingeniería Bioquímica, Pontificia Universidad Católica de Valparaíso (PUCV), Av. Brasil 2085, Valparaíso, Chile

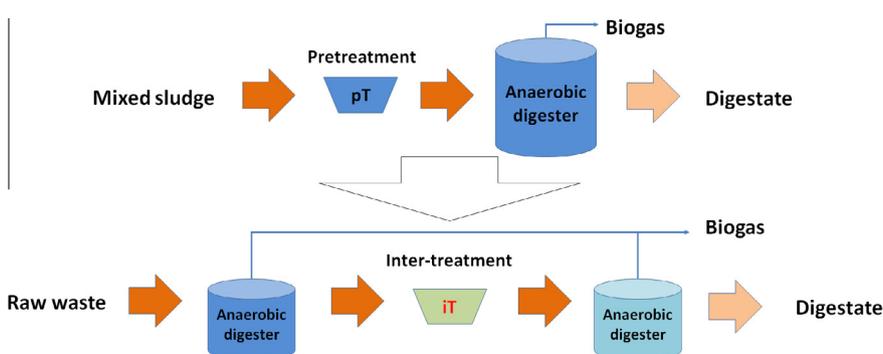
<sup>b</sup> INRIA-Chile, Avenida Apoquindo 2827, Piso 12, Las Condes, Santiago, Chile

<sup>c</sup> Department of Chemical Engineering and Environmental Technology, University of Valladolid, C/ Dr. Mergelina s/n, Valladolid, Spain

## HIGHLIGHTS

- Thermal treatment steam explosion of the digestate was assessed at lab-scale.
- Biochemical methane potential (BMP) test were used to assess the methane production.
- A full-scale digester evaluation was done by using the ADM1 model.
- The best results in the BMP assays were obtained at 180 °C and 200 °C both at 30 min.
- The inclusion of a thermal inter-treatment unit is feasible in a full-scale plant.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 25 February 2016  
 Received in revised form 9 April 2016  
 Accepted 11 April 2016  
 Available online 13 April 2016

### Keywords:

ADM1  
 Anaerobic digestion  
 Biogas  
 Sewage sludge  
 Thermal hydrolysis

## ABSTRACT

The conventional application of thermal pretreatment of sewage sludge has been to apply it prior to the anaerobic digestion. In this study, the thermal treatment of the digestate was assessed at lab-scale under several temperature and time conditions. Biochemical methane potential (BMP) tests were set up to evaluate the methane production kinetic by using the Gompertz modified and the first order equation. A full-scale digester evaluation was done by using the ADM1 model under different scenarios and by using the parameters drawn from the BMP tests. The best results were obtained at 180 °C and 200 °C both at 30 min where an improvement of 50% in the methane yield in regards to raw digestate. Full-scale simulations show that a scenario with two anaerobic reactors with thermal inter-treatment would improve the methane production by 45% and 20% compared to conventional anaerobic digestion and pretreatments followed by anaerobic digestion, respectively.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Pretreatment has become quite an efficient option to improve the biogas potential from solid and semisolid waste. Any pretreat-

ment procedure aims to break down the structure of the particulate organic matter such that the anaerobic biomass may access the organic matter. Cellulose, hemicelluloses, lignin, fat and other complex compounds are affected by the pretreatment condition, such as high temperatures, an acidic or alkali presence, ultrasound, pressure, microwaves, etc. Thermal pretreatment with steam explosion represents one of the most widely used pretreatment techniques for full-scale operations prior to the anaerobic digestion of sewage sludge (Pérez-Elvira and Fdz-Polanco, 2012).

\* Corresponding author at: Escuela de Ingeniería Bioquímica, Pontificia Universidad Católica de Valparaíso (PUCV), Av. Brasil 2085, Valparaíso, Chile.

E-mail addresses: [andres.donoso@ucv.cl](mailto:andres.donoso@ucv.cl), [andres.donoso@inria.cl](mailto:andres.donoso@inria.cl) (A. Donoso-Bravo).

**Table 1**  
Thermal/steam explosion conditions and characterization of the raw and treated MX and DG.

	T (°C)	t (min)	Severity factor log( $R_0$ )	TKN (g/kg)	NH <sub>4</sub> (g/kg)	TS (g/kg)	VS (g/kg)	S <sub>D</sub> (%)	FD
Raw MX	–	–	–	8.0	–	131.9	96.2	–	–
H MX	165	30	3.4	4.0	0.5	61.3	45.3	23.3	2.2
Raw DG	–	–	–	6.0	–	131.7	73.3	–	–
DG-110-0	110	0	0.8	4.0	0.6	82.3	42.8	7.7	1.6
DG-110-10	110	10	1.4	4.0	0.8	81.3	42.2	10.4	1.6
DG-110-30	110	30	1.8	4.0	0.7	71.1	36.4	15.6	1.9
DG-110-50	110	50	2.0	4.0	0.6	77.0	39.2	16.6	1.7
DG-150-0	150	0	1.9	4.0	0.8	93.1	48.5	24.8	1.4
DG-150-10	150	10	2.6	4.0	0.6	80.2	41.9	19.2	1.6
DG-150-30	150	30	3.0	3.0	0.6	71.3	37.3	24.4	1.8
DG-150-50	150	50	3.2	3.0	0.7	64.4	33.5	26.0	2.0
DG-180-0	180	0	2.8	4.0	0.8	90.6	53.2	27.6	1.5
DG-180-10	180	10	3.5	4.0	0.6	74.4	43.0	26.3	1.8
DG-180-30	180	30	3.9	3.0	0.6	63.1	36.7	44.7	2.1
DG-180-50	180	50	4.1	3.0	0.6	55.4	32.0	31.4	2.4
DG-200-0	200	0	3.4	ns	ns	70.1	40.7	nc	1.9
DG-200-30	200	30	4.5	ns	ns	44.5	26.7	nc	3.0
DG-200-50	200	50	4.7	ns	ns	53.1	30.3	nc	2.5

ns: not shown due to measuring issues, nc: not calculated.

In the conventional approach, pretreatment takes place before the anaerobic digestion such that the different fractions of organic matter complex compounds and readily degraded matter undergo the pretreatment. Therefore, the material that is ready to be converted into methane enters the pretreatment despite it does not need to. Afterwards, this pretreated substrate enters the anaerobic reactors where the degradable organic matter is converted into methane leaving, still, a large fraction of not readable organic matter exiting the digester. A new research approach is starting to focus in applying the treatment after the anaerobic digestion process. In this new configuration, the anaerobic digester will convert the readily biodegradable organic matter into methane, in the first step, and the digestate containing the recalcitrant or complex material may then undergo treatment. The “inter-treated” digestate may then enter an anaerobic digester either by recirculating a certain fraction to the anaerobic digester or, as a whole, entering a new AD process. This will reduce the residual organic matter, i.e. less GHG emission and increase the energetic benefit of the treatment. Some research on the treatment of digestate has been carried out, for instance, (Sambusiti et al., 2015), tested thermal (80 °C), alkaline and enzymatic post-treatment, being the last and only one that yielded positive results. The energetic balance was carried out by a preliminary economic and energetic evaluation. Mechanical and thermal pretreatment (autoclave 120 °C and 30 min) of the solid fraction of digested swine slurries was carried out by Menardo et al. (2011). Thermal pretreatment showed good results only with samples that were treated in continuous mode (CSTR reactor) with less than 40 d of HRT. The same pretreatments were assessed by Engler et al. (2015) who investigated the fiber composition variation of digestate upon pretreatment. As noted, there is no clear consensus of the best steam explosion or thermal treatment conditions in order to maximize the treated digestate conversion into biogas.

Biochemical methane potential (BMP) tests are the best experimental platforms used to evaluate the kinetic of the anaerobic degradation of waste, particularly when the hydrolysis is the rate-limiting step. Some valuable kinetic parameters such as the hydrolysis reaction constant and the degradation extent or biodegradability of the substrate may be drawn from a BMP test. However, those kinetic parameters must be evaluated in continuous or semi-continuous operations due to the fact that most of the full scale reactors operate in that mode. The Anaerobic Digestion Model (ADM1) is the most recognized tool which has proven

its capacity to simulate full scale digesters with kinetic parameters obtained in BMP lab tests (Batstone et al., 2009).

The aim of this study was to assess the impact of thermal/steam explosion pretreatment conditions on the enhancement of the residual methane potential of digestate coming from a wastewater treatment plant. The potential full-scale application under several scenarios of this technology was evaluated by using the ADM1 model.

## 2. Material and methods

### 2.1. Inoculum and substrate

The inoculum was obtained from a wastewater treatment plant in Valladolid, Spain with total solid (TS) =  $29.7 \pm 8.8$  g L<sup>-1</sup> and volatile solid (VS) =  $17.0 \pm 5.7$  g L<sup>-1</sup>. This inoculum was degasified (for 3 days) in order to deplete the remaining organic matter (Angelidaki et al., 2009), after that, 5 g L<sup>-1</sup> of sodium bicarbonate was added to the inoculum to assure its buffer capability. The substrates used were digestate (DG) (222.5 g TS kg<sup>-1</sup> and 117.8 g VS kg<sup>-1</sup>) and raw mixed sludge (MX) (27.6 g TS L<sup>-1</sup> and 19.3 g VS L<sup>-1</sup>) obtained from the same wastewater treatment plant. These substrates were diluted and concentrated respectively up to a TS concentration of 12–14%, in order to prepare the samples for the thermal hydrolysis. The main characteristics of the substrates are given next: Digestate: COD = 121.2 g O<sub>2</sub> kg<sup>-1</sup>, Soluble COD = 3.7 g O<sub>2</sub> kg<sup>-1</sup>, TS = 131.7 g kg<sup>-1</sup>, VS = 73.3 g kg<sup>-1</sup>, Nitrogen (TKN) = 0.6 g 100 g<sup>-1</sup>. Activated sludge: COD = 191.4 g O<sub>2</sub> kg<sup>-1</sup>, TS = 131.9 g kg<sup>-1</sup>, VS = 96.2 g kg<sup>-1</sup>, Nitrogen = 0.8 g 100 g<sup>-1</sup>.

### 2.2. Thermal hydrolysis/steam explosion

#### 2.2.1. Pretreatment device

The experiment was carried out in a laboratory-scale thermal steam explosion system. This system consisted of a steam boiler, a 1.5 L total volume hydrolysis reactor (working volume 0.75 L) connected to a flash tank (volume 5 L) equipped with outlet pipes for steam injection and hydrolyzed sludge flushing. The thermal system is equipped with manual valves that control the steam entrance from the boiler and the sludge exit from the reactor to the flash. The pressure, temperature and time of the thermal hydrolysis were measured offline by a manometer, a temperature sensor, and a chronometer respectively. The reactor was loaded

with 0.75 L of raw sludge or digestate, then the steam valve was opened until the desired pressure and temperature was reached (this operation lasted approximately for 3 min). At the end of the reaction time, the decompression valve was opened until all the pressure was released. The hydrolyzed sludge or digestate was collected into the flash tank. The experimental conditions evaluated are shown in Table 1, where “ $t$ ” is the time when the temperature “ $T$ ” was reached. The severity factor was calculated by the Eq. (1) using the total time of reaction for the calculation (heating and reaction time) (Overend et al., 1987). The severity factor (Eq. (1)) is used in the optimization of thermal hydrolysis because this model describes the relationship between the temperature and the time. As explained by Ferreira et al. (2014) this parameter is widely accepted for steam explosion processes despite it does not take into account the flash decompression or any other factor involved.

$$\log R_0 = \log \left( t \cdot \exp \left( \frac{t - 100}{14.75} \right) \right) \quad (1)$$

### 2.2.2. Pretreatment effect

The effect of the thermal/steam explosion treatment was evaluated by estimating the solubilisation of particulate organic matter. The COD solubilisation degree was calculated using Eq. (2).

$$S_D(\%) = \left( \frac{(\text{CODs} - \text{FD}) - \text{COD}_{S_0}}{\text{CODt} - \text{COD}_{S_0}} \right) \cdot 100 \quad (2)$$

where  $\text{COD}_{S_0}$  is the soluble COD concentration of the raw material,  $\text{CODt}$  is the total COD of the raw material,  $\text{CODs}$  is the soluble COD concentration of the hydrolyzed material, and  $\text{FD}$  is an estimation of the dilution of the hydrolyzed sludge, due to the steam entrance into the thermal reactor. This dilution factor was calculated according to Eq. (3), where  $\text{TS}_{\text{raw}}$  is the total solid of the raw sludge, and  $\text{TS}_H$  is the total solid of the hydrolyzed sludge.

$$\text{FD} = \text{TS}_{\text{raw}} / \text{TS}_H \quad (3)$$

## 2.3. Anaerobic biodegradability

### 2.3.1. Batch methane potential test

The batch methane potential tests (BMP) were performed according to Angelidaki et al. (2009) guidelines. These assays were mounted in a glass bottle with 50 ml working volume with 0.5 gVS gVS<sup>-1</sup> as the substrate to inoculum ratio. Blanks were mounted to subtract the biogas produced from the remaining

organic matter that comes with the inoculum. All the tests were carried out at 35 °C in a thermostatic room, equipped with a shaker desk constantly agitated at 150 rpm. All tests were prepared in triplicate. The methane production was calculated at standard conditions (0 °C and 1013.25 mbar) (Eq. (4)).

$$V_{\text{CH}_4} = \left( \frac{\Delta P \cdot V_U \cdot T_{\text{std}}}{T_{\text{test}} \cdot P_{\text{std}}} \right) \cdot \% \text{CH}_4 \quad (4)$$

where  $\Delta P$  is the pressure measured by the manometer (mbar),  $V_U$  is the volume in the headspace (mL),  $T_{\text{std}}$  is the temperature at standard conditions (273.15 K),  $T_{\text{test}}$  is the temperature of the assay (in K),  $P_{\text{std}}$  is the standard pressure (1 atm ~ 1013 mbar) and  $\% \text{CH}_4$  is the percentage of methane in the biogas.

### 2.3.2. Parameter fitting

For parameter determination, the Modified Gompertz (MG) equation (Eq. (5)) and the first order (FO) equation (Eq. (6)) were used. The parameters from the MG equation are mainly used for comparison purposes since it is a model that is being widely employed for anaerobic batch test assessment (Bolado-Rodríguez et al., 2016; Kafle and Chen, 2016; Lobo Baeta et al., 2016). The parameter from the FO equation can be, in turn, used directly with the ADM1 model to evaluate real scale digester operations (Batstone et al., 2009; Souza et al., 2013)

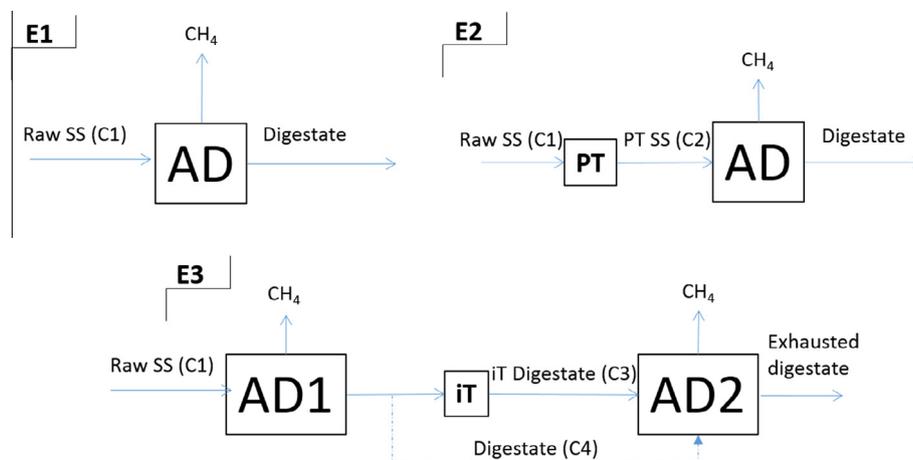
$$B = P_{\infty} \cdot \exp \left( - \exp \left( \frac{Rm \cdot e}{p} (t - \lambda) + 1 \right) \right) \quad (5)$$

$$B = B_{\infty} \cdot (1 - \exp(-k_h(t))) \quad (6)$$

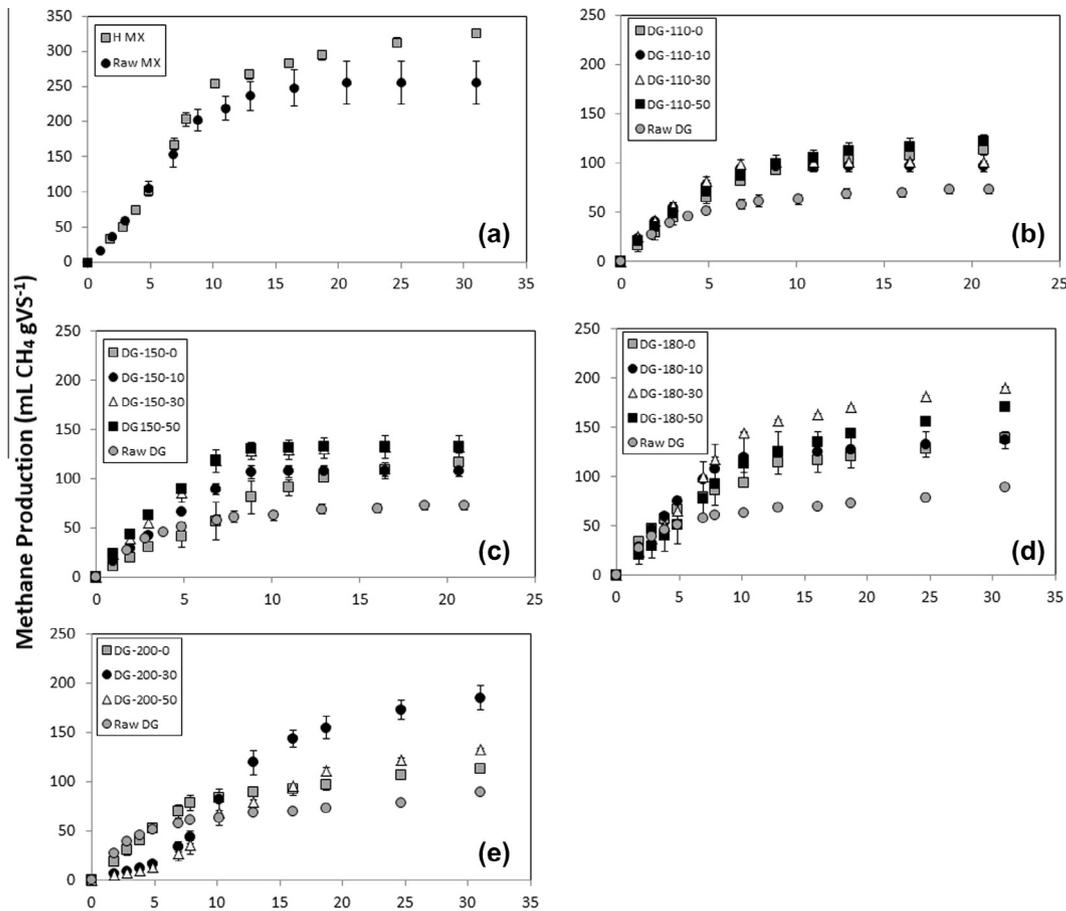
where  $B$  is the biogas produced at time  $t$ ,  $P_{\infty}$  and  $B_{\infty}$  are the maximum biogas production (mL gVS<sup>-1</sup>),  $Rm$  is the maximum biogas production rate (mL d<sup>-1</sup>),  $k_h$  is the first order hydrolysis constant and  $\lambda$  is the lag time (d). For parameter estimation, a simple least squares criterion between the simulated and experimental and Matlab<sup>®</sup> is used for the minimization procedure. The standard deviation was estimated from the covariance matrix of the parameters obtained from the inverse of the Fisher Information Matrix (FIM), which gives a lower bound on the achievable parameter error covariance matrix (CN) (Donoso-Bravo and Fdz-Polanco, 2013).

## 2.4. Analytical methods

COD was measured using the open reflux method (APHA, 2005), TS and VS by gravimetric methods (APHA, 2005) and nitrogen was estimated in a dry basis through the Kjeldahl (2001.11) method



**Fig. 1.** Diagram of evaluated scenarios at full-scale. SS sewage sludge, C Characterization, PT, pretreatment, iT inter treatment. C1, C2, C3 and C4 correspond to the specific characterization of the raw sewage sludge, pretreated sewage sludge inter-treated and raw digestate.



**Fig. 2.** Evolution of the methane production of: (a) raw and thermal hydrolyzed mixed sludge, (b)–(e) raw and hydrolyzed digestate at several conditions of temperature and time.

(AOAC, 2012). The biogas production and the methane content were measured by a hand held digital manometer and a gas chromatograph (VARIAN 3800) respectively.

## 2.5. Full-scale assessment based on mathematical modeling (ADM1)

### 2.5.1. Scenarios selection

In order to estimate and assess the best system configuration at full-scale, a modeling approach was carried out. The Anaerobic Digestion Model 1 (ADM1) has been used to model full-scale plant (Batstone et al., 2009; Ozkan-Yucel and Gökçay, 2010; Shang et al., 2005). The full scale application of conventional pretreatment (PT) and inter-treatment (iT) were assessed by using ADM1 at mesophilic conditions. Inter-treatment is the assigned name given to the treatment applied between two anaerobic digestion processes. Three scenarios were considered, namely:

E1: Conventional anaerobic digestion of raw sewage sludge.

E2: Raw sewage sludge pretreatment followed by anaerobic digestion.

E3: Inter-treatment of digestate followed by a second anaerobic digestion process.

Each scenario is depicted in Fig. 1.

The ADM1 was run until steady state conditions were reached. Different initial conditions were tested in order to rule out any effect of these upon the outputs. Some performance parameters such as the specific methane production, in terms of reactor volume as well as in terms of the VS added and removed, were used for the assessment.

### 2.5.2. Models parameters and ADM1 adjustment

The general modification suggested by Rosen and Jeppsson (2006) were also used in this study. The parameters were kept as suggested by the ADM1 report, although the low and upper limit of the pH inhibition function for  $H_2$  consumers was changed, as suggested ADM1 for primary sludge, to 6.7 and 5.8 for the upper and lower limit, respectively. Furthermore, a VS output was also incorporated, together with the normal COD output, by using conversion COD/mass ratios from the generalized mineralization equation (Christensen, 2010). The COD/mass ratio of the inerts and biomass was taken from Batstone et al. (2010). The composite concentration ( $X_c$ ) was set equal to zero such that the particulate carbohydrates, proteins, lipids and inert were the inputs condition to the ADM1 model. The elimination of the disintegration step originally considered in the ADM1 has been lately suggested as necessary due to all the disadvantages that the use of a two-hydrolyses step brought, especially for sewage sludge approaches (Batstone et al., 2015). ADM1 was implemented and solved in Matlab® 2015b.

## 3. Results and discussion

### 3.1. Thermal/steam explosion effect on the digestate (DG)

The characterization of the raw (MX), hydrolyzed sludge (H-MX), raw and thermal treated digestate (DG) at the different conditions is showed in the Table 1, where it can be seen that the hydrolyzed substrate was diluted by the effect of the steam

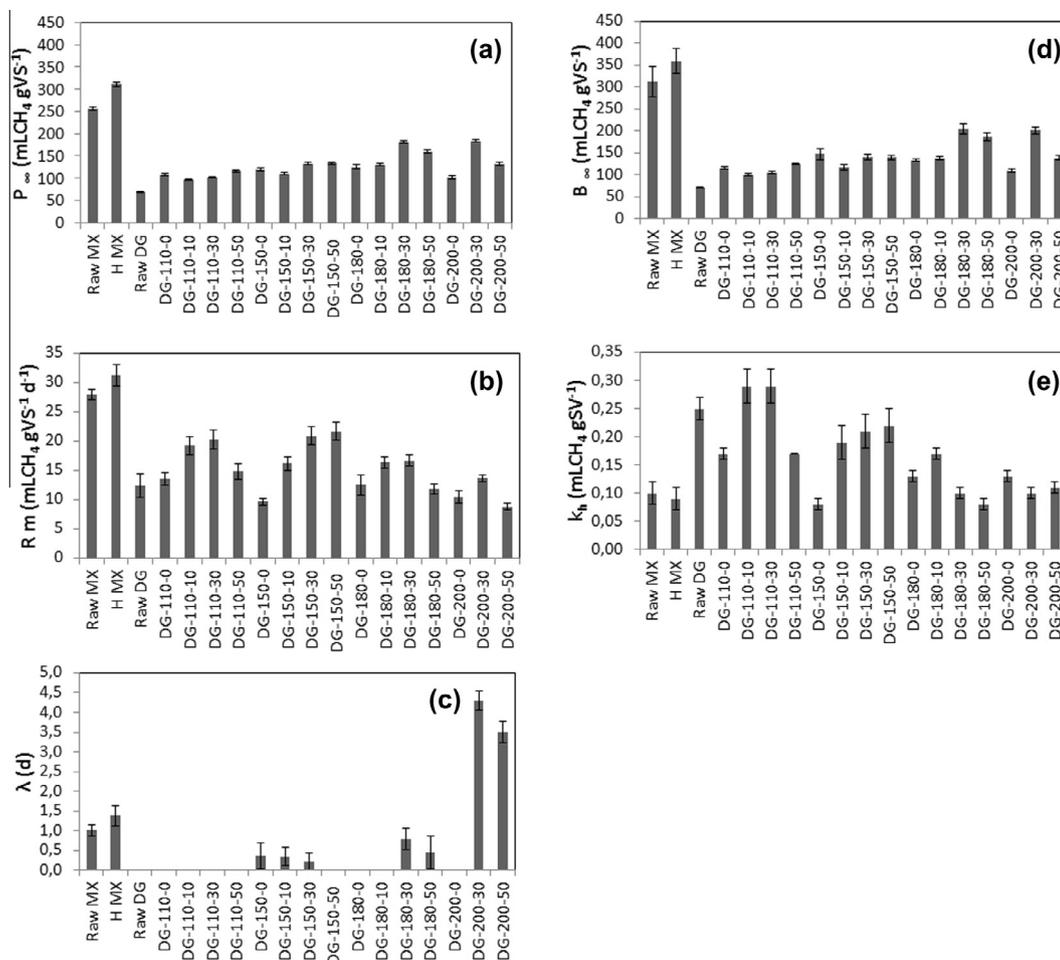


Fig. 3. Parameters values obtained by adjusting the Modified Gompertz model (a–c) and the first order model (d and e) to the methane production curves.

Table 2

Summary of the input condition of the modeling evaluation.

	Unit	C1	C2	C3	C4
Total COD	g L <sup>-1</sup>	80	80	80	80
Soluble COD		8	36.8	49.3	2.5
Particulate COD		72	43.2	30.7	77.6
Biodegradability	%	57.9	66.6	38.0	13.5
$k_h$	d <sup>-1</sup>	0.098	0.092	0.097	0.248

ranging from 1.4 to 3.0 times the volume of the initial sludge loading volume depending, above all, on the pretreatment time. On the other hand, the solubilisation degree of COD improved at higher severity factors. In regards to the MX, the values obtained in agreement with those that have been reported for sewage sludge between 25% and 40% (Bougrier et al., 2007; Donoso-Bravo et al., 2011). In regards to the digestate, the treatment increases the solubilisation which also increases as the severity increases. The  $S_D$  is also similar to the values that have been reported for sewage sludge; however, it is worth mentioning that to our knowledge there is no reported information on solubilisation variation on the treated digestate sludge. The TKN was decreased at higher severity factor principally due to the dilution, because by multiplying the TKN values with the FD gives nearly 6 g kg<sup>-1</sup> which is the value of raw digested sludge or 8 g kg<sup>-1</sup> in the case of raw activated sludge. Finally, the ammonia concentration remained constant between 1 and 1.4 g kg<sup>-1</sup> (multiplying by the FD to discard the dilution effect).

## 3.2. BMP test

### 3.2.1. Methane production kinetic

The results of the cumulative methane production from the anaerobic digestion of digestate (DG), thermally treated and untreated, and mixed activated sludge, thermally treated (H-MX) and raw (MX), are presented in Fig. 2. As can be observed, all the conditions used had a positive effect in terms of improving the methane production compared to the raw substrates. The shape of the curves was in general the typical saturation profiles with a rapid generation of methane from the beginning up to reaching a methane production plateau. The exceptions were the BMP test for condition DG-200-0 and DG-200-30, which were the most severe pretreatment conditions, where a lag-phase and a sigmoid profile was obtained. This type of curve is typical when some inhibitory compounds or recalcitrant organic matter is present in the test, which agrees with the type of organic compounds that are typically found when sewage sludge undergo thermal pretreatment at very high severity conditions (Pérez-Elvira et al., 2006). These results were evaluated more precisely through the estimation of the parameters of the models presented above. The parameters of these models are presented in the Fig. 3 and the curve fitting are depicted in appendices section. The parameter which represents the maximum methane potential in the activated sludge ( $B_{\infty}$  and  $P_{\infty}$  for first order and Gompertz respectively), showed a 21% of improvement in the case of hydrolyzed activated sludge. Similar values of improvement, with a methane yield ranging from 180 to 250 mLCH<sub>4</sub> gVS<sup>-1</sup>, were found by Donoso-Bravo

et al. (2011) and Cano et al. (2014) who obtained nearly the same values for  $P_{\infty}$  sludge at similar conditions using sludge from the same wastewater treatment plant. The parameter  $k_h$  decreased slightly and the parameter  $R_m$  augmented slightly. The lag time ( $\lambda$ ) for the hydrolyzed activated sludge augmented slightly in comparison to raw sludge; however, both lag phase remained low (<2 days).

On other hand the methane yields,  $B_{\infty}$  and  $P_{\infty}$ , for the thermal treated DG increases as the severity of the thermal treatment increases. The major enhancement was observed for conditions DG-180-30 and DG-200-30 with around 1.5-fold improvement the value of the raw DG. Regarding the hydrolysis, no improvement was observed in the case of the  $k_h$ , which, in fact, showed an important reduction of this value in regards to the raw DG in most of the cases. Similar results are obtained for the parameter  $R_m$  where the best conditions were DG-110-10, DG-110-30 and DG-150-30 obtaining up to 1.75 times the value of raw digested sludge. The above is also corroborated by the lag time ( $\lambda$ ) which it remains under a day for almost all conditions except for the most severe ones (DG-200-30 and DG-200-50) this could be also explained by the formation of more complex and recalcitrant compounds (Ferreira et al., 2014).

It is worth to point out, the unexpected large difference of the  $k_h$  values for MX, H-MX and raw DG. One explanation to this lies on the fact that the material in MX and H-MX is presented in a more complex way and the inoculum has to adapt to it, which it actually does quickly. In contrast, the inoculum is already adapted for digestate because digestate is in fact the same inoculum.

### 3.2.2. General mass balance

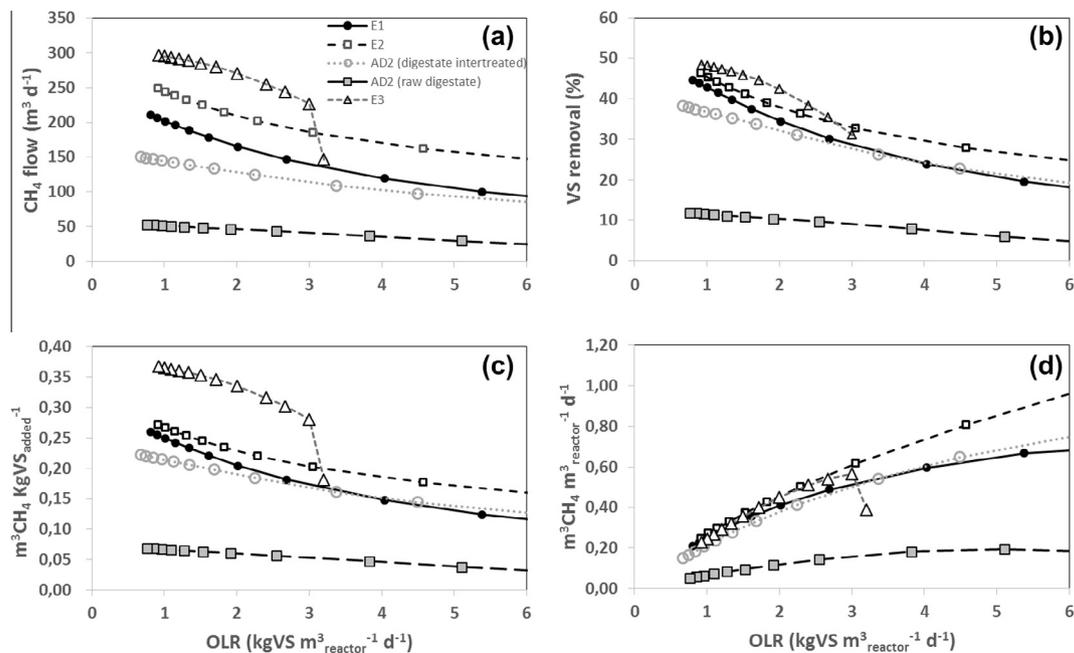
According to the results obtained, a general balance in batch conditions to estimate the biodegradability of three different scenarios was carried out (Fig. 1). The biodegradability was calculated by dividing the methane yield obtained in the experiments and the theoretical methane yield, i.e.  $350 \text{ mLCH}_4 \text{ COD}^{-1}$  or  $703.5 \text{ mLCH}_4 \text{ VS}^{-1}$  for the activated sludge in this case. The RT (reaction time) means an approximation of the time that lead to the maximum methane potential on the BMP assays. In order to do the balance

for E3, the result obtained at condition DG-180-30 was chosen due to its high methane yield and less severity than DG-200-30 which had yielded similar results. The first scenario (E1) showed a biodegradability of 36% at an RT of 25 days. This value agrees with Cano et al. (2014) where 34% of biodegradability was obtained (calculating it in the same way) using also mixed sewage sludge from the same wastewater plant. Values ranging from 35%, similar to values obtained in the present study, to 75% were obtained by Mottet et al. (2010) which demonstrated that this biodegradability value strongly depends on the type of WWTP the sludge sample comes from. In the case of E2, a 44% of biodegradability was attained at a similar RT as the previous scenario. This alternative has been widely studied and applied in full-scale plants (for instance Cambi process). Mottet et al. (2010) observed the same biodegradability increase of around 20% under similar pretreatment conditions. Finally, E3 showed that a 62% of biodegradability could be achieved with a RT of 25 d for the first digester and 20 d for the second one. This represents an important increase in the methane recovery and VS removal in comparison to the conventional E1. Treatment of digestate has been evaluated especially with agricultural and mixed-manure digestate. Positive results in terms of enhancement the methane potential have been obtained with enzymatic treatment (Sambusiti et al., 2015) mechanical treatment (Lindner et al., 2015) and ultrasound (Boni et al., 2016).

### 3.3. Full scale simulation results

#### 3.3.1. Input conditions

C1, C2, C3 and C4 (Fig. 1) correspond to the specific characterization of the raw sewage sludge, pretreated sewage sludge inter-treated and raw digestate, respectively, which will correspond to the inlet conditions of the model. The lab characterization allows one to establish the ratio between particulate and soluble COD which is 9, 1.2, 0.6 and 31.8 for C1, C2, C3 and C4, respectively. Furthermore, BMPs will provide the inert fraction of the organic matter and the hydrolytic constant, the only kinetic parameter that will be change during the evaluation. Table 2 presents the input



**Fig. 4.** Steady state behavior of the anaerobic reactors fed with raw sewage sludge (E1), with thermal treated sewage sludge (E2), raw digestate (AD2: blue line), inter-treated digestate (AD2: grey line) and two digester systems with inter-treatment (E3). (a) Methane flow (b) volatile solid removal (c) specific methane production (d) volumetric methane production. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

conditions used for the modeling application. The characterization procedure developed by Souza et al. (2013) and some experimental results from Donoso-Bravo et al. (2011) were used to fix some inlet conditions that were not measured such as the organic matter breaking down for both particulate and soluble compounds, which were set as follows: carbohydrates 20%, proteins 65% and lipids 15%.

3.3.2. Reactor performance under different scenarios

BMP tests offer a good platform to have a first approximation of the benefit of any kind of improvement of the anaerobic biodegradability. However, the results that can be obtained in a full-scale continuous reactor can turn out to be different; however, by using the ADM1 and the parameters drawn from the BMP test, a quite appropriate estimation of the reactor performance in continuous mode may be obtained.

Fig. 4 shows the steady state results of the full-scale plant based on the ADM1 at different organic load rates (OLR). It is worth mentioning that the OLR values are higher compared to the usual values applied in full-scale anaerobic digestion which is due to the high organic matter concentration (around 80 g L<sup>-1</sup> of total COD instead of 50–60 g L<sup>-1</sup>) considered for this simulation part. Scenarios E1, E2, E3 and the operation of a second anaerobic digester (AD2) feed with raw and inter-treated digestate, are depicted in Fig. 4. Each OLR was evaluated by changing the digester volume assuming a constant inlet flow of 15 m<sup>3</sup> d<sup>-1</sup> of sludge. The inlet flow of the second digester was also set at 15 m<sup>3</sup> d<sup>-1</sup>, since it

was assumed that the thickener, where the digestate is concentrated, and the inter treatment where the digestate is diluted (apart from being treated) yield the same amount of waste and total organic matter of 80 g L<sup>-1</sup>.

As expected the difference between the conventional treatment of raw (E1) and pretreated sludge (E2) is important, around 24–25% of improvement of the total methane produced, and consequently in the VS removal, are observed. At low OLR applied in continuous reactor, i.e., around 1–2 kgVS m<sup>3</sup> d<sup>-1</sup> the VS removal agrees with what was obtained in the BMP test. In regards to the specific performance parameters (c and d) the same trend is observed, E2 outperforms E1, and this difference gets bigger as the OLR increases. The performance of a second anaerobic digester is enhanced notoriously if it is fed with inter-treated digestate instead of raw digestate. Overall all the parameters double or triple in regards to the digester treating raw digestate. Therefore, in a real WWTP where some units are usually unused, either anaerobic digester or other units that can be easily adapted for AD, inter-treatment may offer a great opportunity for enhancing the biogas production i.e., increase the self-production of the energy requirement of the plant, the organic matter removal while keeping the pathogens elimination of a traditional pretreatment (Gurief et al., 2012). It has to be kept in mind, that likewise the conventional thermal pretreatment, an inter-treatment process incorporation will be feasible as long as a co-generation unit is implemented such that the generated heat is used for the inter-treatment process heating (Pérez-Elvira and Fdz-Polanco, 2012).

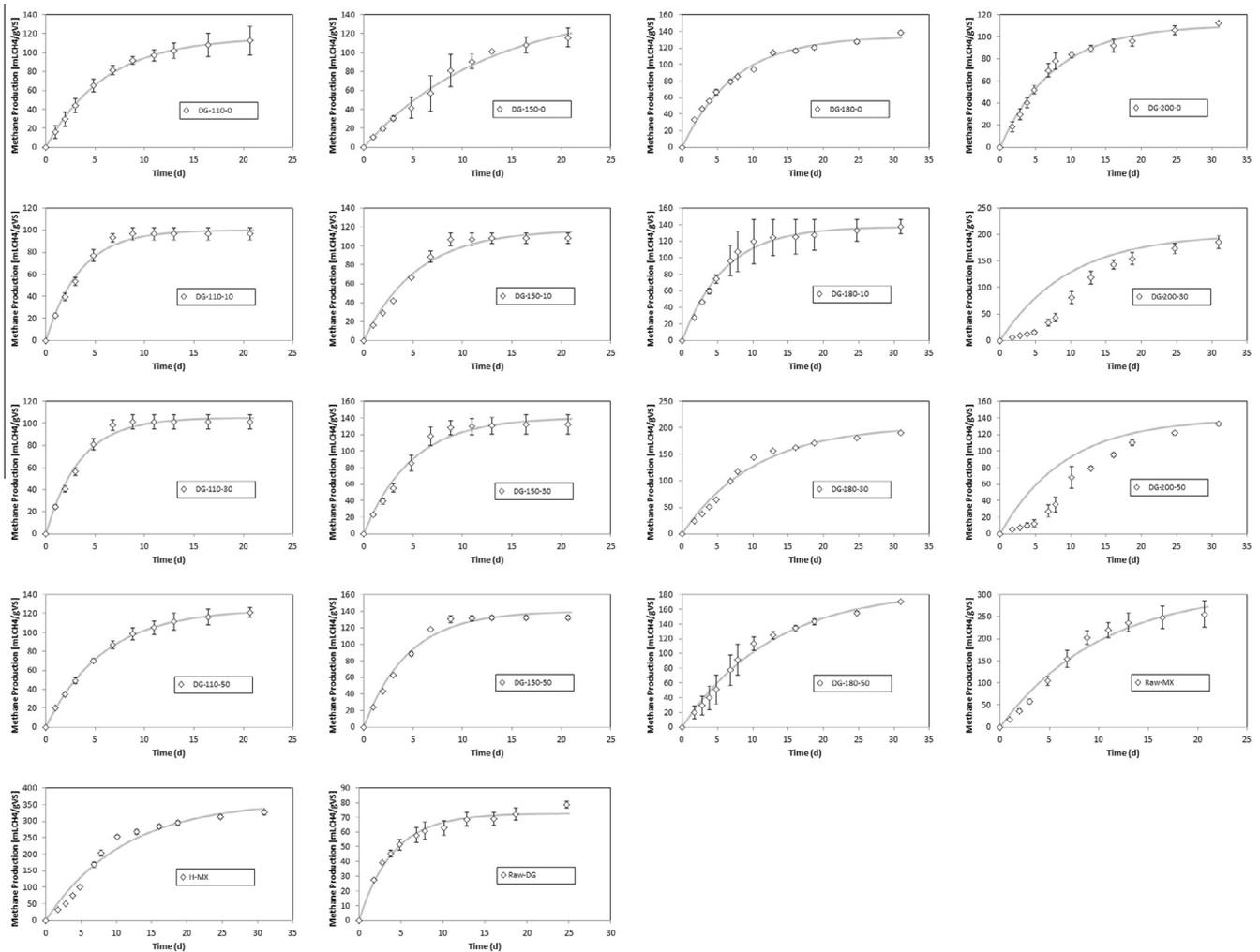


Fig. A1. First order equation fitting.

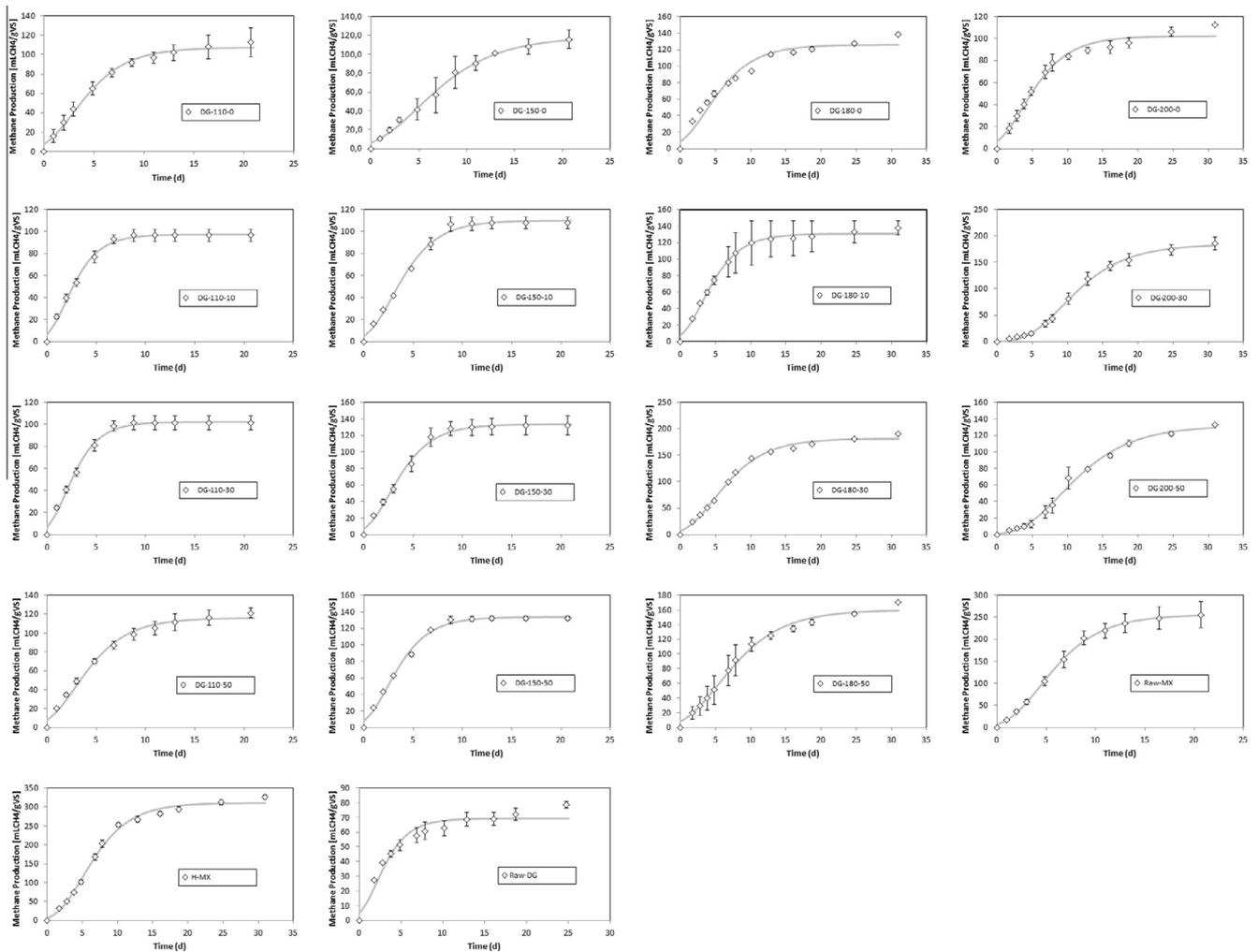


Fig. A2. Gompertz modified equation fitting.

In order to get a more fair comparison, the performance of E3 (AD + it + AD2) was also plotted, by summing the results of a conventional AD (E1) plus the AD2 fed with inter treated sludge. Overall, this system outperforms the conventional pretreatment (E2) configuration, except in the specific volumetric methane production, which values are basically the same. As previously mentioned, this would not be an issue if spare units at the WWTP may be employed for this purpose. The E3 line stops until the volume of the AD2 is too small and the system collapses (the methanogens are washed out from the digester), which basically means that E1 is the continuation of the performance of the E3. It worth to point out that the volume of AD1 was fixed at the conventional conditions of anaerobic digestion of sewage sludge; however, under this new scenario, the volume of AD1 may be optimized and reduced since the main goal of the first biodegradation is to easily remove degradable organic which can be carried out in a shorter time than the conventional digestion period.

The results can be further improved by considering more possible scenarios, for instance, part of the extracted liquid from the thickener, which contains large amount of soluble organic matter, can be recirculated to the AD1 inlet and only the solid fraction undergoes inter-treatment. Another potential scenario is a different combination of primary and secondary sludge that undergo pretreatment. Also, a certain fraction of the treated digestate may be returned to the digester entrance and mix with the inlet raw sewage sludge. This may be an alternative when no other anaero-

bic digestion unit is available. Nevertheless, this study provides a global view of the incorporation of this type of treatment into the current WWTP configuration.

#### 4. Conclusion

In this study the impact of thermal inter-treatment of digestate was evaluated by using a BMP test along with a full-scale anaerobic system modeling. The maximum production methane rate was improved especially at low severity conditions, while the hydrolysis rate constant was, overall, negatively affected as severity factor increases. The global biodegradability of mixed sewage sludge rises up to 62% from 36% when the digestate is thermally treated and then digested again. A scenario with two anaerobic reactors with a thermal inter-treatment unit would improve the generated methane in 45% and 20% compared to a conventional anaerobic digestion and pretreatment plus anaerobic digestion of mixed sewage sludge, respectively.

#### Acknowledgements

This study was funded by Fondecyt Initiation project n° 11130462 and supported by CIRIC -INRIA-Chile (EP BIONATURE) through Innova Chile Project. The authors would like to express their gratitude to Jaime Benito Cortijo and Araceli Crespo Rodriguez for all their technical support in this study.

## Appendix A

See Figs. A1 and A2.

## References

- Angelidaki, I., Alves, M., Bolzonella, D., Borzacconi, L., Campos, J.L., Guwy, A.J., Kalyuzhnyi, S., Jenicek, P., van Lier, J.B., 2009. Defining the biomethane potential (BMP) of solid organic wastes and energy crops: a proposed protocol for batch assays. *Water Sci. Technol.* 59, 927–934.
- AOAC, 2012. Official Methods of Analysis of AOAC International, 19th ed.
- APHA, 2005. Standard Methods for the Examination of Water and Wastewaters, 21st ed. American Public Health Association, Washington.
- Batstone, D.J., Balthes, C., Barr, K., 2010. Model assisted startup of anaerobic digesters fed with thermally hydrolysed activated sludge. *Water Sci. Technol.* 62, 1661–1666.
- Batstone, D.J., Puyol, D., Flores-Alsina, X., Rodríguez, J., 2015. Mathematical modelling of anaerobic digestion processes: applications and future needs. *Rev. Environ. Sci. Bio/Technol.*
- Batstone, D.J., Tait, S., Starrenburg, D., 2009. Estimation of hydrolysis parameters in full-scale anaerobic digesters. *Biotechnol. Bioeng.* 102, 1513–1520.
- Bolado-Rodríguez, S., Toquero, C., Martín-Juárez, J., Travaini, R., García-Encina, P.A., 2016. Effect of thermal, acid, alkaline and alkaline-peroxide pretreatments on the biochemical methane potential and kinetics of the anaerobic digestion of wheat straw and sugarcane bagasse. *Bioresour. Technol.* 201, 182–190.
- Boni, M.R., Amato, E.D., Polettini, A., Pomi, R., Rossi, A., 2016. Effect of ultrasonication on anaerobic degradability of solid waste digestate. *Waste Manage.* 48, 209–2017.
- Bougrier, C., Delgenès, J.P., Carrère, H., 2007. Impacts of thermal pre-treatments on the semi-continuous anaerobic digestion of waste activated sludge. *Biochem. Eng. J.* 34, 20–27.
- Cano, R., Nielfa, A., Fdz-Polanco, M., 2014. Bioresource technology thermal hydrolysis integration in the anaerobic digestion process of different solid wastes: energy and economic feasibility study. *Bioresour. Technol.* 168, 14–22.
- Christensen, T., 2010. *Solid Waste Technology and Management*, 2. Wiley.
- Donoso-Bravo, A., Fdz-Polanco, M., 2013. Anaerobic co-digestion of sewage sludge and grease trap: assessment of enzyme addition. *Process Biochem.* 48, 936–940.
- Donoso-Bravo, A., Pérez-Elvira, S., Aymerich, E., Fdz-Polanco, F., 2011. Assessment of the influence of thermal pre-treatment time on the macromolecular composition and anaerobic biodegradability of sewage sludge. *Bioresour. Technol.* 102, 660–666.
- Engler, N., Scholwin, F., Sutter, R., Nelles, A., 2015. Performance enhancement of biogas digesters by post-treatment and recirculation of digestate. In: Cossu, R., He, P., Kjeldsen, P., Matsufuji, Y., Reinhart, D., Stegmann, R. (Eds.), 15th International Waste Management and Landfill Symposium. CISA, Sardinia.
- Ferreira, L.C., Souza, T.S.O., Fdz-Polanco, F., Pérez-Elvira, S.I., 2014. Thermal steam explosion pretreatment to enhance anaerobic biodegradability of the solid fraction of pig manure. *Bioresour. Technol.* 152, 393–398.
- Gurief, N., Nielsen, B., Ole, F., Boyd, J., Kline, M., 2012. Enhanced digestion with EXELYSTM-DLD™ – a direct pathway to a sustainable and cost effective wastewater treatment plant. *Proceeding of the Water Environment Federation, Residuals and Biosolids*, pp. 1001–1010.
- Kafle, G.K., Chen, L., 2016. Comparison on batch anaerobic digestion of five different livestock manures and prediction of biochemical methane potential (BMP) using different statistical models. *Waste Manage.* 48, 492–502.
- Lindner, J., Zielonka, S., Oechsner, H., Lemmer, A., 2015. Effects of mechanical treatment of digestate after anaerobic digestion on the degree of degradation. *Bioresour. Technol.* 178, 194–200.
- Lobo Baeta, B.E., Sousa Lima, D.R., Herrera Adarme, O.F., Alves Gurgel, L.V., de Aquino, S.F., 2016. Optimization of sugarcane bagasse autohydrolysis for methane production from hemicellulose hydrolyzates in a biorefinery concept. *Bioresour. Technol.* 200, 137–146.
- Menardo, S., Balsari, P., Dinuccio, E., Gioelli, F., 2011. Thermal pre-treatment of solid fraction from mechanically-separated raw and digested slurry to increase methane yield. *Bioresour. Technol.* 102, 2026–2032.
- Mottet, A., François, E., Latrille, E., Steyer, J.P., Déléris, S., Vedrenne, F., Carrère, H., 2010. Estimating anaerobic biodegradability indicators for waste activated sludge. *Chem. Eng. J.* 160, 488–496.
- Overend, R.P., Chornet, E., Gascoigne, J.A., 1987. Fractionation of lignocelluloses by steam-aqueous pretreatments [and discussion]. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* 321, 523–536.
- Ozkan-Yucel, U.G., Gökçay, C.F., 2010. Application of ADM1 model to a full-scale anaerobic digester under dynamic organic loading conditions. *Environ. Technol.* 31, 633–640.
- Pérez-Elvira, S.I., Fdz-Polanco, F., 2012. Continuous thermal hydrolysis and anaerobic digestion of sludge. *Energy integration study. Water Sci. Technol.* 65, 1839–1846.
- Pérez-Elvira, S.I., Nieto Diez, P., Fdz-Polanco, F., 2006. Sludge minimisation technologies. *Rev. Environ. Sci. Bio/Technol.* 5, 375–398.
- Rosen, C., Jeppsson, U., 2006. Aspects on ADM1 implementation within the BSM2 framework 2. *The IWA Benchmark Simulation Models*, 1–34.
- Sambusiti, C., Monlau, F., Ficara, E., Musatti, A., Rollini, M., Barakat, A., Malpei, F., 2015. Comparison of various post-treatments for recovering methane from agricultural digestate. *Fuel Process. Technol.* 137, 359–365.
- Shang, Y., Johnson, B.R., Sieger, R., 2005. Application of the IWA anaerobic digestion model (ADM1) for simulating full-scale anaerobic sewage sludge digestion. *Water Sci. Technol.* 52, 487–492.
- Souza, T.S.O., Carvajal, A., Donoso-Bravo, A., Peña, M., Fdz-Polanco, F., 2013. ADM1 calibration using BMP tests for modeling the effect of autohydrolysis pretreatment on the performance of continuous sludge digesters. *Water Res.* 47, 3244–3254.