Long-term hydrolytic capacity evaluation of a thermophilic anaerobic digester treating sewage sludge

Andres Donoso-Bravo, Sara Pérez-Elvira, Alain Vande Wouwer
and Fernando Fdz-Polanco

ABSTRACT

This study presents an evaluation of the hydrolytic activity of a continuous thermophilic anaerobic reactor in long-term operation. The hydrolytic coefficient was estimated by fitting a three-reaction model of the anaerobic digestion process with experimental data obtained from a pilot thermophilic digester operated for about 2 years. The model fitting and the cross-validation indicate that this model can represent the behavior of the system in a proper way; moreover, the results show a variation of the hydrolytic capacity of the system throughout the evaluation period. The increase in the hydrolytic coefficient is in agreement with the increase in the organic load applied to the reactor, which shows the capacity of the continuous reactor to select populations according to the input conditions of the system.

Key words | biogas, cross-validation, modeling, thermophilic digester

Andres Donoso-Bravo (corresponding author)
Alain Vande Wouwer
Automatic Control Laboratory,
University of Mons,
31 Boulevard Dolez,
B-7000 Mons,
Belgium
E-mail: andres.donosobravo@umons.ac.be

Sara Pérez-Elvira
Fernando Fdz-Polanco
Department of Chemical Engineering and
    Environmental Technology,
University of Valladolid,
Prado de la Magdalena s/n,
47011, Valladolid,
Spain

NOMENCLATURE

X_0 particulate organic matter (g L^{-1})

X_1 acidogens population (g L^{-1})

X_2 methanogens population (g L^{-1})

S_1 soluble organic matter (g L^{-1})

S_2 acetic acid equivalent (g L^{-1})

K_1–K_6 stoichiometric coefficients

k_0 hydrolytic constant (d^{-1})

r_0 hydrolysis rate (g L^{-1}d^{-1})

r_1 acidogenesis rate (g L^{-1}d^{-1})

r_2 methanogenesis rate (g L^{-1}d^{-1})

μ_1 specific growth rate of the acidogens (d^{-1})

μ_2 specific growth rate of the methanogens (d^{-1})

μ_{1M} maximum specific growth rate of the acidogens (d^{-1})

K_{SA} affinity constant of the acidogens (g L^{-1})

μ_{2M} maximum specific growth rate of the methanogens (d^{-1})

K_{SM} affinity constant of the methanogens (g L^{-1})

K_{IM} inhibition constant of the methanogens (g L^{-1})

ξ state variable

ξ_0 state variable in the system input

f_B biodegradability of the substrate

D dilution rate (d^{-1})

IC   inorganic carbon (mmol L^{-1})

Z alkalinity (mmol L^{-1})

INTRODUCTION

Sewage sludge from wastewater treatment plants (WWTPs) is one of the most important substrates used in anaerobic digestion. In Europe, the total annual potential of biogas production from the anaerobic digestion of sewage sludge is estimated at around 200 billion m^3 (Appels *et al.* 2008). Mesophilic anaerobic treatment has been mostly used, however, the capacity and size of thermophilic digesters have increased significantly in the last decade (de Baere *et al.* 2010). The anaerobic digestion process at thermophilic conditions (~55 °C) increases the biogas production as the reaction rates involved in the process increase, achieving better results compared with a mesophilic reactor (Watts *et al.* 2006; Bolzonella *et al.* 2007). Moreover, thermophilic conditions increase the pathogen removal minimizing the disinfection requirements. The latter has been pointed out as the main cost-benefit advantage of the thermophilic process over the mesophilic one (Suryawanshi *et al.* 2010).

The anaerobic degradation of sewage sludge is rate-limited by the hydrolysis of the particulate organic matter (Vavilin *et al.* 2008; Donoso-Bravo *et al.* 2009), thus the estimation of the parameters related to this process has been a subject of increasing interest, especially under mesophilic conditions (Batstone *et al.* 2009; Ge *et al.* 2011). Hence, further research is required to evaluate the hydrolysis kinetics in thermophilic conditions.

Normally long-term pilot or full-scale reactor operations have to deal with important fluctuations of both input flow and substrate concentration due to the daily variation in the sewage sludge quality together with the variations in the solid content of the influent. This may become an important issue in thermophilic operation as this process is less stable than the conventional mesophilic one (Suryawanshi *et al.* 2010). Ferrer *et al.* (2010) assessed the long-term performance and stability of a thermophilic reactor focusing on the determination of compounds-indicators at different solid retention times (SRT) and organic load rates (OLR) in a laboratory-scale system. On the other hand, long-term operation in a continuous reactor can lead to population changes (selection) or physiological adaptation, as relatively steady ambient conditions are applied (Grady *et al.* 1996). Moreover, fluctuations in culture conditions (dilution rate, food to microorganism ratio, presence or lack of a readily biodegradable substrate) lead to various metabolic states as well as varying numbers of acclimated organisms in the overall population. In this context, there is a lack of research about anaerobic biomass acclimation in long-term operations of anaerobic digesters. The objective of this study is to evaluate the behavior of a pilot thermophilic reactor with variable input conditions and to estimate its hydrolysis capability throughout the operation period. For this purpose, a simplified mathematical model of the anaerobic digestion process is used.

MATERIALS AND METHODS

Experimental equipment and data

The experimental data were obtained from a pilot scale thermophilic anaerobic digester (continuous stirred-tank reactor (CSTR)-type, $55 \pm 1°C$) with a total volume of 100 L. The reactor was fed with thickened mixed sludge (5% DS) that came from the domestic WWTP of Valladolid, Spain. Every load of sludge for feeding was conserved at $4\,°C$ and lasted for 3 days. Samples of sludge, from both the feeding tank and the digester outlet, were taken daily and characterized in terms of solids and organic matter content (chemical oxygen demand, COD), both determined according to standard methods (APHA 1995). The biogas production was measured by liquid displacement in an inverted cylinder equipped with an electro-valve to release the biogas when the volume reached 550 ± 10 mL. Biogas composition was measured by gas chromatography through the injection of 1 mL of sample directly into the column.

The digester was continuously operated for nearly two years, and the feeding load was progressively increased by reducing the hydraulic retention time (HRT) from 40 to 2 days. Figure 1 shows the evolution of the digester in terms of HRT and OLR during the whole operation period (600 days). The average composition of the raw sludge was as follows: TS 52.2 ± 6.5 g L^{-1}, VS 36.2 ± 4.5 g L^{-1}, total COD 53.1 ± 2.7 g L^{-1} and soluble COD 2.8 ± 1.3 g L^{-1}. The average conditions of each period were: (1) HRT 80-5 d and OLR 0.07–0.5 g COD L^{-1} d^{-1} (2) HRT 20 and OLR 0.6 g COD L^{-1} d^{-1} (3) HRT 6 d and OLR 4.2 g COD L^{-1} d^{-1} (4) HRT 3 d and OLR 10 g COD L^{-1}d^{-1} (5) HRT 2 d and OLR 15.2 g COD L^{-1}d^{-1}. On day 169, the digester collapsed due to a clogging problem, thus the digester was reseeded and the operation started over. Figure 1 shows that the OLR fluctuates more than the HRT due to the constant variations in the organic matter concentration of the influent.

Mathematical model

Model assumptions and description

A two-population and three-reaction model (Donoso-Bravo *et al.* 2009) adapted from the two-reaction model developed by Bernard *et al.* (2001) is used to evaluate the overall behavior of the reactor. The acidogenic population (X_1) hydrolyses X_0 to S_1 which is suitable to be acidified (Equation (1)) and
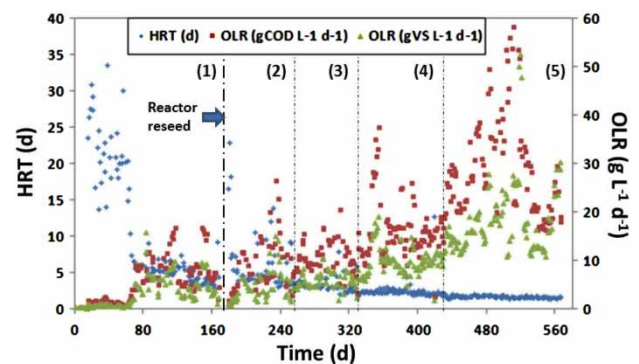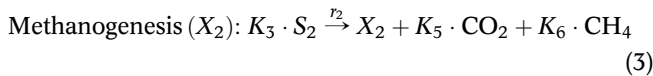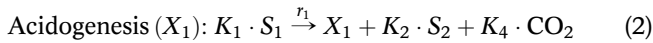

Figure 1 | Input conditions of the thermophilic anaerobic reactor during the whole operation period.

then it transforms S_1 to S_2 in the acidogenic process, with microbial growth (Equation (2)). Then, the methanogenic population (X_2) transforms S_2 into biogas (CH_4 and CO_2), with microbial growth (Equation (3)):

$$\text{Hydrolysis } (X_1): X_0 \xrightarrow{r_0} S_1 \tag{1}$$

$$\text{Acidogenesis } (X_1): K_1 \cdot S_1 \xrightarrow{r_1} X_1 + K_2 \cdot S_2 + K_4 \cdot CO_2 \tag{2}$$

$$\text{Methanogenesis } (X_2): K_3 \cdot S_2 \xrightarrow{r_2} X_2 + K_5 \cdot CO_2 + K_6 \cdot CH_4 \tag{3}$$

With respect to the reaction rates, first-order, Monod and Haldane–type equations are considered for hydrolysis, acidogenesis and methanogenesis reactions respectively (Equations 4–6):

$$r_0 = k_0 \cdot X_0 \tag{4}$$

$$r_1 = \mu_1 \cdot X_1 = \left(\mu_{1M} \cdot \frac{S_1}{K_{SA} + S_1} \right) \cdot X_1 \tag{5}$$

$$r_2 = \mu_2 \cdot X_2 = \left(\mu_{2M} \cdot \frac{S_2}{K_{SM} + S_2 + (S_2^2/K_{IM})} \right) \tag{6}$$

A simple mass balance for a continuous reactor is shown in Equation (7):

$$\frac{d\xi}{dt} = K \cdot r(\xi) + D(\xi_0 \cdot f_B - \xi) \tag{7}$$

$$\xi = \begin{bmatrix} X_0 \\ X_1 \\ X_2 \\ S_1 \\ S_2 \\ IC \\ Z \end{bmatrix} \quad K = \begin{bmatrix} -1 & 0 \\ 1 & 0 \\ 0 & 1 \\ -K_1 & 0 \\ K_2 & -K_3 \\ K_4 & K_5 \\ 0 & 0 \end{bmatrix} \quad r(\xi) = \begin{bmatrix} r_0 \\ r_1 \\ r_2 \end{bmatrix} \quad \xi_0 = \begin{bmatrix} X_{0i} \\ 0 \\ 0 \\ S_{1i} \\ 0 \\ IC_i \\ Z_i \end{bmatrix}$$

Gaseous streams are expressed as a function of some state variables as described in Bernard et al. (2001).

Model implementation

Simulations and the optimization procedure were performed in Matlab®. The input conditions of the system were taken from the influent characterization (flow and COD). The system was solved as many times as influent characterizations were performed and the final values of the state variables of each run were used as the initial conditions for the next one. These final values were saved in order to be used in the optimization procedure. The values of the stoichiometric coefficients and the kinetic parameters were estimated and approximated from Siegrist et al. (2002) and Bernard et al. (2001) (Table 1). Setting the initial conditions is not as critical as in a batch test, as in continuous systems the initial conditions have a negligible effect, especially in the case of long-term operation evaluations.

Sensitivity analysis

Sensitivity analysis (SA) attempts to assess the influence of the parameters (also called factors) of a model (i.e. kinetic parameters, stoichiometric coefficients, initial conditions, etc.) on its outputs (i.e. the measured variables). In this case, the root of the mean squared (relative) prediction error (RMSE), as given by Equation (8), was used to compare the results obtained in a nominal or baseline situation with the ones obtained by varying ±50% of the set of parameters. A continuous reactor operated for 20 days at varying flow and organic matter concentration was simulated for the SA.

$$\text{RMSE} = \sqrt{\frac{1}{N} \sum_{t=1}^{N} \left(y_{nom,i} - y_{sim,i} \right)^2} \tag{8}$$

Table 1 | Parameters and stoichiometric coefficient values used for the sensitivity analysis and the their sensitivity with respect to the biogas production

Parameter	Nominal value	Reference	RMSE +50%	−50%
k_0	0.2	Siegrist et al. (2002)	3.760	5.921
μ_{1M}	16		0.003	0.007
μ_{2M}	5		0.028	0.075
K_{S1}	0.2		0.006	0.003
K_{S2}	5		0.037	0.037
K_{I2}	25		<0.001	<0.001
k_1	42.1	Bernard et al. (2001)	8.261	24.86
k_2	116.5		10.85	10.84
k_3	268		7.205	21.646
k_4	50.6		1.567	1.564
k_5	343		4.616	4.590
k_6	453		6.197	6.230
f_B	0.5	Estimated	6.271	6.248

where y_{nom} and y_{sim} are the nominal and the evaluated simulation, respectively, and N corresponds to the number of data points. The nominal simulation was performed with the parameters shown in Table 1.

Kinetic parameters determination

The whole operation trial was divided in five periods; in each of them the parameter estimation was performed. Each period is divided in two sets of data, the first one for model fitting and the second for cross-validation. A direct-search procedure based on the Nelder–Mead algorithm and the least-squares criterion (Equation (9)), were used for the optimization:

$$J(\theta) = \min \sum_{t=1}^{N} \left(y_{exp}(t) - y_{sim}(t, \theta) \right)^2 \big|_{\theta_0 = \theta_L} \quad (9)$$

where J is the objective function, y_{exp} is the obtained value from measurements and θ represents the parameters to be determined and N is the number of measurements.

The variance of the measurement errors can be estimated from Equation (10) evaluated at the optimum, as:

$$\sigma^2 = \frac{J(\hat{\theta})}{N - n_\theta} \quad (10)$$

where $J(\theta)$ is the value of the objective function evaluated at the optimum and n_θ is the number of estimated parameters.

The covariance matrix of the parameter errors can be approximated by a second-order expansion around the estimated parameters (Equation (11)) (Vanrolleghem & Keesman 1996). This Hessian matrix (H) can be drawn

from Levenberg-Marquardt or Newton algorithms (by-product of *Fmincon-Matlab*®) used for the optimization process (Vande Wouwer *et al.* 2006):

$$C_H(\theta) = 2\sigma^2 [H(\theta)]^{-1} \quad \text{where} \quad H = \left| \frac{\partial^2 J(\theta)}{\partial \theta \partial \theta^T} \right|_{\hat{p}} \quad (11)$$

If this covariance matrix is available, an approximation of the standard deviation of the parameters can be estimated through Equation (12):

$$\sigma(\theta_i) = \sqrt{C_H} \quad (12)$$

RESULTS AND DISCUSSION

Parametric sensitivity analysis and parameter selection

As expected in a continuous operation, the stoichiometric coefficients are the most influential parameters for the biogas production and, overall, the kinetic parameters have a little influence upon this output (Table 1). However, among the kinetic parameters the hydrolytic constant, by far, has the most important influence on the biogas production. Hence, the other parameters can be fixed considering the values reported in the literature. The biodegradable fraction also has a relatively important impact as it indicates the degradation extent of the substrate.

The data from day 1 to 169, period 1 (until the system had to be rebooted and reseeded), were used to calibrate the most influential parameters, i.e. k_1, k_2, k_3 and k_6. From that point onwards, the hydrolytic coefficient, k_0, is estimated for the periods 2, 3, 4 and 5, assuming that the
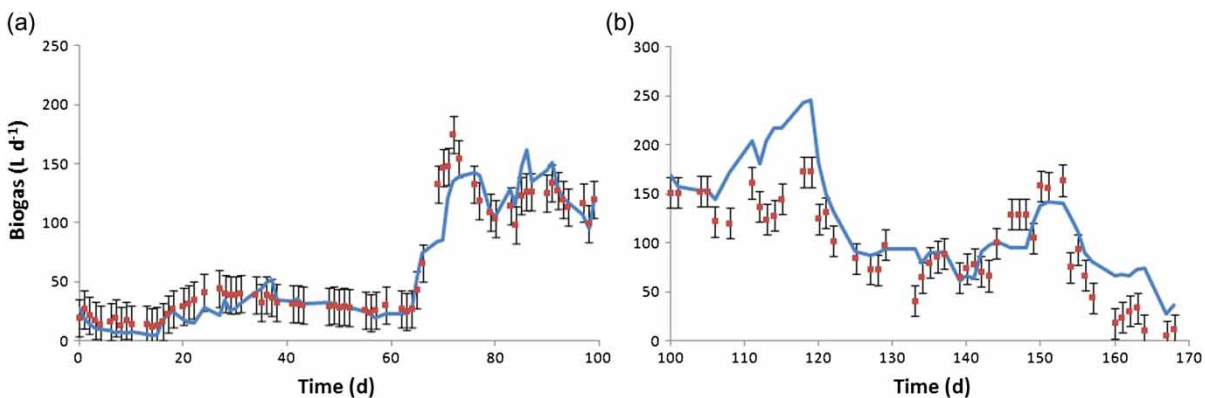

Figure 2 | Determination of the stoichiometric coefficients of the model (a) model fit (b) cross-validation during period 1 of operation.

stoichiometric coefficients remain constant. The biodegradable fraction of the total particulate organic matter, f_B, was fixed at 0.5 (i.e. 50% of the particulate organic matter is anaerobically biodegradable). This fraction is the typical value reported for waste activated sludge degradation in anaerobic digesters (Batstone et al. 2009; Ge et al. 2011). Fixing this value alleviates some potential parameter identification problems (Batstone et al. 2009).

Stoichiometric coefficient calibration

The results of the stoichiometric coefficient determination and model validation are shown in Figure 2. The estimated values of the coefficients k_1, k_2, k_3 and k_6 are: 43, 127, 286 and 828 mmol g^{-1}, respectively.

The fitting process (Figure 2(a)) went well as the biogas production was predicted quite well by the extended model.
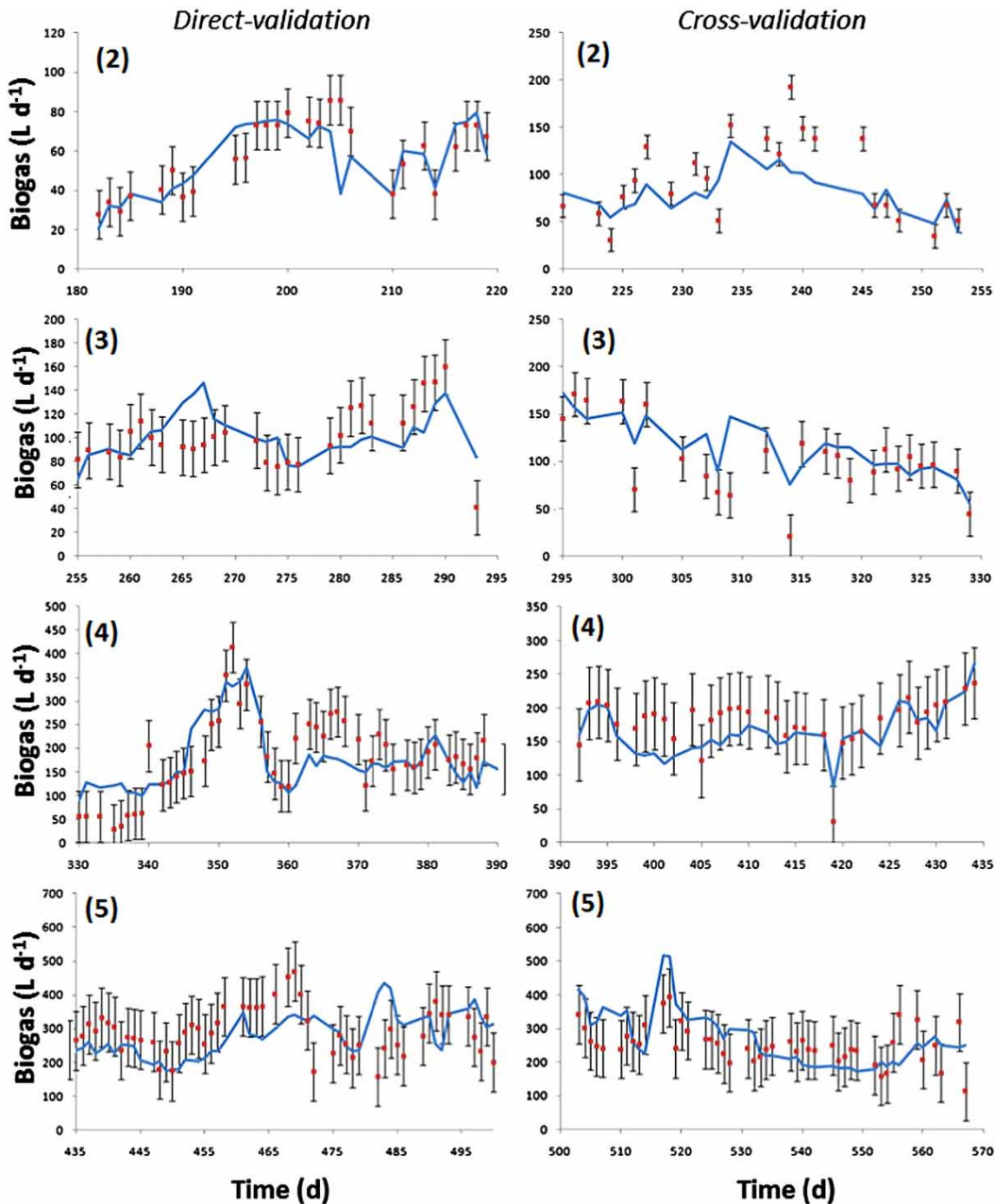

Figure 3 │ Model fit and cross-validation during periods 2 to 5 of operation.

The cross-validation (Figure 2(b)) shows, in general, very few discrepancies over relatively short time periods with both over- and under-prediction, which probably demonstrates good model calibration.

Overall, the estimated values are close to those originally reported by Bernard *et al.* (2011), as the first three coefficients present an increase of around 10% compared with the nominal ones. A notably different result is however obtained for k_6, which is almost 83% higher than the nominal one. This value is also much higher than the one reported in mesophilic conditions by Lopez & Borzacconi (2009) using a highly biodegradable substrate such as malting effluent. Despite the fact that the sewage sludge used in this study has a low fraction of soluble organic matter, the thermophilic biomass was able to reach a high yield for methane production which confirms one of the main advantages of thermophilic digestion.

Hydrolytic capacity of the anaerobic biomass

The results of the parameters determination and validation from periods 2 to 5 are shown in Figure 3, where the first column shows the fitting results and the second one shows the cross-validation.

In direct validation there is a good agreement between the model prediction and the experimental data in all the operation periods. With respect to the cross-validation, globally the model output mimics the experimental results reasonably well. However, some significant discrepancies between model prediction and the experimental data are occasionally observed. In general, large changes in the biogas production are not well predicted by the model which can be due to the underlying modeling assumptions and simplifications. For instance, primary sludge is extremely variable in composition (different types of organic compounds) with variable biodegradability, however the model considers the organic matter entering the system only as soluble and particulate compounds. Moreover, the influent flow (one of the model inputs) is considered constant over each sampling period whereas the flow can vary during the day due to the complex rheological properties of the sludge and the presence of different solid compounds (such as hair and paper) in the sludge, and a perfect fit may only be possible with idealized and constant influent compositions.

With regards to the hydrolytic capacity evolution of the thermophilic biomass the values estimated for all periods were: (2) $0.111 \pm 0.012\,\mathrm{d}^{-1}$ (3) $0.350 \pm 0.030\,\mathrm{d}^{-1}$ (4) $0.617 \pm 0.092\,\mathrm{d}^{-1}$ and (5) $0.765 \pm 0.037\,\mathrm{d}^{-1}$. In general terms, it can be noticed that there is a continuous increase

in the hydrolytic capacity of the anaerobic population. In period 3, the hydrolysis constant value increases by 215% with respect to the previous one. Likewise, the increase of this coefficient for periods 4 and 5 is 76% and 24%. The values of k_0, in the periods 2 and 3, are slightly smaller than those obtained by Blumensaat & Keller (2005) and Siegrist *et al.* (2002), although in the same order of magnitude. With regards to period 4 and 5, the attained hydrolysis coefficients are comparable with the ones obtained by Ge *et al.* (2011) who used a TPAD (temperature phase anaerobic digestion, i.e. a short thermophilic pre-treatment followed by conventional mesophilic digestion) system fed with waste activated sludge at different pre-treatment temperatures. It is known that changes in culture conditions such as increasing and/or variable dilution rates might promote changes in the metabolic states, as well as the selection of the most active biomass. However, and as it was stated for long chain fatty acids (LCFA) adaptation (Palatsi *et al.* 2010), it is not clear whether these changes are due to the enrichment of hydrolytic microorganisms (population adaptation) or to a physiological adaptation of the existing microorganisms.

Figure 4 shows a plot with the estimated values of k_0 as a function of the OLR. The high linear correlation between these two parameters indicates the dependence of the process performance on the hydrolytic capacity of the biomass in the studied operation conditions.

Despite the fact that microbial adaptation has been a subject of study in aerobic systems, kinetic parameter variation, due to the biomass acclimation in AD, has been scarcely evaluated. The few studies that have been done have focused on the biomass adaptation evaluation to LCFA as they are considered important inhibitors of the process (Palatsi *et al.* 2010).
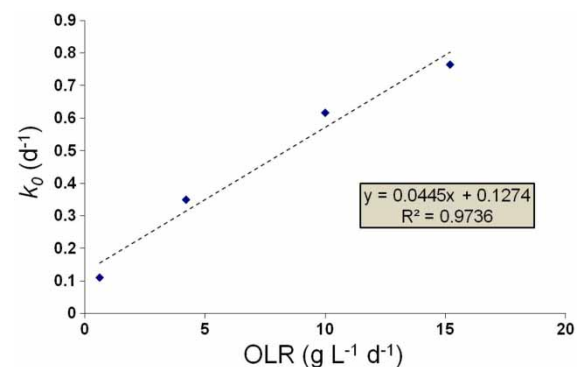
Figure 4 | Linear regression between k_0 and the applied OLR.

CONCLUSION

A simplified model of anaerobic digestion may be used for the behavior prediction of a thermophilic anaerobic digester in the treatment of sewage sludge. Continuous reactor operations with variable input conditions provide proper conditions for modeling application and identification. Some kinetic parameters, as in this case the hydrolytic coefficient, may vary during a long-term operation, which indicates the enrichment or adaptation of the microbial population.

ACKNOWLEDGEMENTS

REFERENCES

APHA, AWWA, WPCP 1995 *Standard Methods for the Examination of Water and Wastewater*. American Water Works Association/American Public Works Association/Water Environment Federation, 19th edition, Washington, DC.

Appels, L., Baeyens, J., Degreve, J. & Dewil, R. 2008 Principles and potential of the anaerobic digestion of waste-activated sludge. *Progr. Energ. Combust. Sci.* **34** (6), 755–781.

Batstone, D. J., Tait, S. & Starrenburg, D. 2009 Estimation of hydrolysis parameters in full-scale anerobic digesters. *Biotechnol. Bioeng.* **102** (5), 1513–1520.

Bernard, O., Hadj-Sadok, Z., Dochain, D., Genovesi, A. & Steyer, J. P. 2001 Dynamical model development and parameter identification for an anaerobic wastewater treatment process. *Biotechnol. Bioeng.* **75** (4), 424–438.

Blumensaat, F. & Keller, J. 2005 Modelling of two-stage anaerobic digestion using the IWA Anaerobic Digestion Model No. 1 (ADM1). *Water Res.* **39** (1), 171–183.

Bolzonella, D., Pavan, P., Zanette, M. & Cecchi, F. 2007 Two-phase anaerobic digestion of waste activated sludge: effect of an extreme thermophilic prefermentation. *Ind. Eng. Chem. Res.* **46**, 6650–6655.

de Baere, L. A., Mattheeuws, B. & Velghe, F. 2010 State of the art of anaerobic digestion in Europe. 12th World Congress on Anaerobic Digestion (AD12), Guadalajara, Mexico, October 31st to November 4th, 2010.

Donoso-Bravo, A., Retamal, C., Carballa, M., Ruiz-Filippi, G. & Chamy, R. 2009 Influence of temperature on hydrolysis, acidogenesis and methanogenesis in anaerobic digestion: parameter identification and modeling application. *Water Sci. Technol.* **60** (1), 9–17.

Ferrer, I., Vazquez, F. & Font, X. 2010 Long term operation of a thermophilic anaerobic reactor: process stability and efficiency at decreasing sludge retention time. *Bioresour. Technol.* **101** (9), 2972–2980.

Ge, H. Q., Jensen, P. D. & Batstone, D. J. 2011 Temperature phased anaerobic digestion increases apparent hydrolysis rate for waste activated sludge. *Water Res.* **45** (4), 1597–1606.

Grady, C. P. L., Smets, B. F. & Barbeau, D. S. 1996 Variability in kinetic parameter estimates: a review of possible causes and a proposed terminology. *Water Res.* **30** (3), 742–748.

Lopez, I. & Borzacconi, L. 2009 Modelling a full scale UASB reactor using a COD global balance approach and state observers. *Chem. Eng. J.* **146**, 1–5.

Palatsi, J., Illa, J., Prenafeta-Boldu, F. X., Laureni, M., Fernandez, B., Angelidaki, I. & Flotats, X. 2010 Long-chain fatty acids inhibition and adaptation process in anaerobic thermophilic digestion: batch tests, microbial community structure and mathematical modelling. *Bioresour. Technol.* **101** (7), 2243–2251.

Siegrist, H., Vogt, D., Garcia-Heras, J. & Gujer, W. 2002 Mathematical model for meso- and thermophilic anaerobic sewage sludge digestion. *Environ. Sci. Technol.* **36** (5), 1113–1123.

Suryawanshi, P. C., Chaudhari, A. B. & Kothari, R. M. 2010 Thermophilic anaerobic digestion: the best option for waste treatment. *Crit. Rev. Biotechnol.* **30** (1), 31–40.

Vande Wouwer, A., Renotte, C., Queinnec, I. & Bogaerts, P. 2006 Transient analysis of a wastewater treatment biofilter - distributed parameter modelling and state estimation. *Math. Comput. Model. Dyn. Syst.* **12** (5), 423–440.

Vanrolleghem, P. A. & Keesman, K. J. 1996 Identification of biodegradation models under model and data uncertainty. *Water Sci. Technol.* **33** (2), 91–105.

Vavilin, V. A., Fernandez, B., Palatsi, J. & Flotats, X. 2008 Hydrolysis kinetics in anaerobic degradation of particulate organic material: an overview. *Waste Manag.* **28**, 939–951.

Watts, S., Hamilton, G. & Keller, J. 2006 Two-stage thermophilic–mesophilic anaerobic digestion of waste activated sludge from a biological nutrient removal plant. *Water Sci. Technol.* **53** (8), 149–157.