Modeling the anaerobic digestion of autohydrolysis-pretreated secondary sludge: first-order and ADM1 comparison

T. S. O. Souza*, A. Carvajal*, A. Donoso-Bravo**, M. Peña* and F. Fdz-Polanco*

* Department of Chemical Engineering and Environmental Technology, University of Valladolid, C/ Dr. Mergelina s/n, 47011, Valladolid, Spain
(E-mail: *tsouza@iq.uva.es*)
** Escuela de Ingeniería Bioquímica, Facultad de Ingeniería, Pontificia Universidad Católica de Valparaíso, General Cruz 34, Valparaíso, Chile

Abstract
First-order and ADM1 modeling approaches were compared to evaluate the effects of a novel pretreatment technique, autohydrolysis, in the anaerobic digestion of waste activated sludge (WAS). Hydrolysis constant rates were calibrated using data from biochemical methane potential (BMP) tests and validated using data from continuous digesters fed with raw and pretreated WAS. Results indicated that the ADM1 is more suitable for predicting the effect of the pretreatment than a first-order approach. The ADM1 was also capable of successfully representing slowly-biodegradable organics consumption and limiting step changes promoted by the pretreatment.

INTRODUCTION

Waste activated sludge (WAS) management is of major importance in wastewater treatment plants, and the application of pretreatment techniques for improving anaerobic digestion (AD) of WAS is a suitable procedure for optimizing treatment systems. In this regard, the autohydrolysis pretreatment is a novel technique that combines a low-thermal ($55^{o}C$) heating with microaerobic conditions in order to stimulate WAS to produce hydrolytic enzymes, increasing biodegradability and methane production (Gavala et al., 2003; Carvajal, 2012).

Modeling is a useful tool to assess aspects of biosystems not easily extracted from physicochemical analyses alone. Models vary widely from classical approaches, such as first-order modeling, to more complex and complete approaches, such as the IWA Anaerobic Digestion Model No. 1 (ADM1) (Batstone et al., 2002). Model calibration needs a data source, and in the case of AD models, biochemical methane potential (BMP) tests may be a suitable choice due to its frequency in sludge digestion practices. For hydrolytic-limited processes, BMP tests provide the possibility to estimate the degradation extent and the first-order hydrolysis rate coefficient (Jensen et al., 2011). Aside from its usefulness in first-order approaches, BMP tests could also be an interesting source of data for calibrating ADM1 hydrolysis parameters.

The aim of this study was to compare first-order and ADM1 approaches to evaluate the effects of the autohydrolysis pretreatment on AD of sewage WAS, using BMP tests as a data source for hydrolysis parameters estimation. Calibrated parameters were employed for cross-validation, using experimental data of two continuous digesters fed with both types of WAS.

MATERIAL AND METHODS

Waste characteristics and continuous digesters

Sewage WAS was obtained from the wastewater treatment plant of Valladolid, Spain, and was concentrated up to 8% of total solids. The autohydrolysis pretreatment was held for 12 h at $55\pm0.5^{o}C$ with a minimum oxygen concentration of 1.25 mmol $O_2.L^{-1}$ in the headspace of 2-L

continuously agitated bottles. The pretreatment had a great effect on the solubilization of organics, and thus an increase in soluble COD (COD_s) (from 3.0 to 27.0 $g.L^{-1}$) was observed, while total COD (COD_t) (83.4 $g.L^{-1}$), total solids (TS (80.7 $g.L^{-1}$) and total volatile solids (TVS) (61.7 $g.L^{-1}$) remained nearly constant. Two identical 20-L anaerobic digesters (D_1, D_2) were simultaneously operated to treat raw and autohydrolysis pretreated WAS, respectively. Both were mixed by sludge recirculation and were operated at 35^oC. Four hydraulic retention times (HRT) were applied during 220 days of operation, after an acclimation period, in the following order: 17, 15, 13 and 20 d.

BMP tests and analytical methods

BMP tests were carried out at a substrate/inoculum (S/I) ratio of 0.5. Inoculum was obtained from a mesophilic digester treating WAS. Tests were conducted at 35 ± 1^oC for 25 days, period during which the biogas production was measured by a pressure transmitter. Solids and COD were measured according to the *Standard Methods for the Examination of Water and Wastewater* (2005). Biogas composition was determined by gas chromatography (Varian CP-3800 CG).

ADM1 implementation and inputs

The ADM1 was implemented in Matlab/Simulink®, following the guidelines and suggested parameters of Batstone et al. (2002) (with exception of the ones calibrated in this study) and the modifications proposed by Rosén and Jeppsson (2006). COD inputs were defined fractionating COD_t in its biodegradable and inert parts (using results from BMP tests), and considering the effects of autohydrolysis on organic matter solubilization. COD corresponding to carbohydrates, proteins and lipids were determined based on previous sludge characterization. For calibration with BMP tests, 50% of inert COD was allocated to the variable X_c (composites) of the ADM1, to account for slowly-biodegradable organic matter. Biomass inputs were defined based on maximum growth rate of each microbial community (μ_{max}), as a rough approximation for BMP tests, and based on previous simulations for continuous validation.

Calibration and validation

A first-order equation (Eq. 1) was adjusted to BMP tests data to obtain degradation extent (B_0) and a first-order apparent hydrolysis rate coefficient (k_h).

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

where B is the biogas produced and t is the time. ADM1 hydrolysis parameters (k_{dis}, k_{hydch}, k_{hydpr}, k_{hydli}) were calibrated using the same data. For calibration, a least square cost-function measuring the differences between experimental and simulated values was minimized. Cross-validation was performed using continuous operation data from D_1 and D_2 and calibrated parameters for the corresponding type of feeding (raw and pretreated WAS).

RESULTS AND DISCUSSION

Calibration of hydrolysis parameters

First-order and ADM1 calibrations both resulted in good fits to BMP tests data. (Table 1). The first-order simulations presented the typical stabilization of the curve after the initial period of the assays (Fig. 1). On the other hand, ADM1 simulations curves showed a crescent behavior all along, following the experimental data tendencies. Therefore, ADM1 simulations were a much more realistic approach regarding slowly-biodegradable organic matter consumption.

Table 1. Calibrated first-order and ADM1 hydrolysis constant rates for BMP tests.

	First-order		ADM1				
	k_h (d^{-1})	R^2	k_{dis} (d^{-1})	k_{hydch} (d^{-1})	k_{hydpr} (d^{-1})	k_{hydli} (d^{-1})	R^2
Raw WAS	0.28	0.9809	0.24	2.38	4.42	1.49	0.9854
Pretreated WAS	0.40	0.9797	5.60	0.72	1.07	3.91	0.9764

Estimated hydrolysis constant rates, both for first-order and ADM1, increased for autohydrolysis pretreated WAS (Table 1). Since hydrolysis in the ADM1 is divided in two steps (disintegration and hydrolysis), differences were observed as well for the limiting step controlling the global hydrolysis in the ADM1. For raw WAS, the limiting step stayed at disintegration (k_{dis}=0.24 d^{-1}), and for pretreated WAS, the limiting step moved forward to hydrolysis of carbohydrates (k_{hydch}=0.72 d^{-1}). The observed limiting step change is in accordance with what would be expected for autohydrolysis pretreatment. This technique acts at the disintegration of the microbial flocs matrix, making organic matter more bioavailable for the next steps of AD (Carvajal, 2012). ADM1 calibrated hydrolysis constant rates seemed to mathematically corroborate this phenomenon, showing that the pretreatment increases the disintegration kinetics of complex organic particles. This is an additional information that can be provided by the ADM1 and not by first-order approaches.
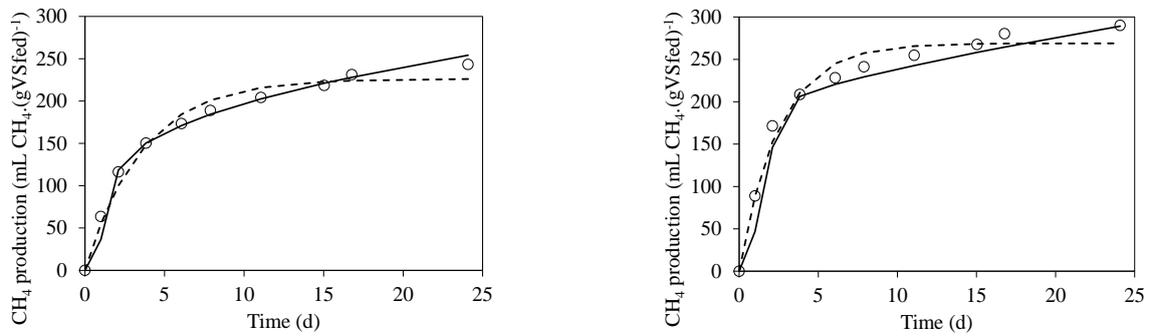

Figure calibrated hydrolysis constant rates for (a) raw WAS and (b) pretreated WAS.

Continuous digesters cross-validation

In general, ADM1 simulations followed reasonably the behavior of the continuous digesters D_1 and D_2, while first-order simulation diverged especially for D_2, as can be seen in Fig. 2. The models seemed to overestimate CH_4 production at different levels, depending on HRT applied.
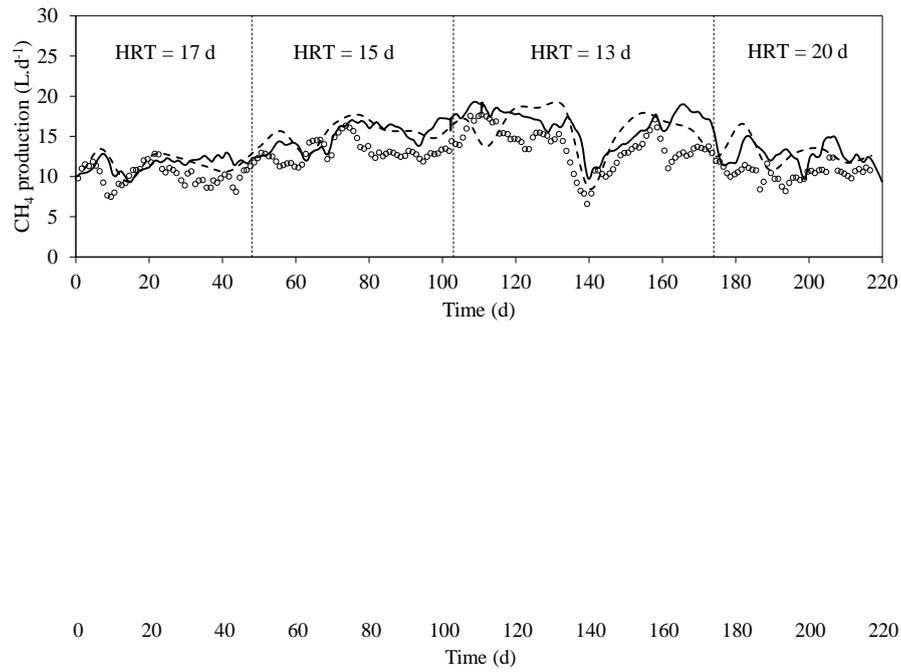

Figure 2. CH_4) experimental data,

Overestimation was more evident during operation with HRT of 15 and 13 d (Fig. 2). In those regions, it was observed that when there was a peak in the experimental CH_4 production and a subsequent drop, the simulated curves followed the event, but sustained higher productions for a longer period than the actual data. This may be due to the fact that inlet data fed to the models was not as numerous as CH_4 production data. Therefore, fluctuations in the inlet affected the results produced by the models much more than observed in reality.

It is evident in Fig. 2 that the ADM1 simulations were more successful in predicting the behavior of the digesters than first-order approaches. First-order simulations presented greater fluctuations and overestimated greatly the CH_4 production for D_2 (Fig. 2b). When comparing the autohydrolysis pretreatment effect prediction provided by each approach, the ADM1 simulations predicted much more accurately the increasing in CH_4 production promoted by the pretreatment than the first-order approach (Table 2). First-order simulations overpredicted excessively this effect for HRTs of 15, 13 and 20 d. These results indicate that, although first-order could represent reasonably the behavior of a digester fed with raw WAS, ADM1 simulations were more suitable for predicting the effect when the autohydrolysis pretreatment was applied.

Table 2. Pretreatment effect on the increasing of CH_4 production for experimental data and simulated results.

	HRT (d)			
	17	15	13	20
Experimental (%)	15.9	13.5	10.0	23.9
Simulated first-order (%)	15.0	18.8	23.0	29.0
Simulated ADM1 (%)	13.2	15.6	12.5	19.0

CONCLUSIONS
A modeling approach using the ADM1 is more suitable for predicting effects of the autohydrolysis pretreatment on the AD of WAS than a first-order approach, while the latter could only predict reasonably the AD of raw WAS. The ADM1 was also capable of successfully representing slowly-biodegradable organics consumption and limiting step changes promoted by the pretreatment.

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