

Available online at www.sciencedirect.com

SciVerse ScienceDirect

journal homepage: www.elsevier.com/locate/issn/15375110

Research Paper

Kinetic studies on the anaerobic degradation of soluble and particulate matter in potato wastewater

Ignacio Durruty^{a,*}, Noemí E. Zaritzky^b, Jorge F. González^a

^a Grupo de Ingeniería Bioquímica, Departamento de Ingeniería Química, Facultad de Ingeniería, Universidad Nacional de Mar del Plata, Juan B. Justo 4302, 7600 Mar del Plata, Bs. Aires, Argentina

^b Centro de Investigación y Desarrollo en Criotecnología de Alimentos (CIDCA, UNLP-CONICET), Facultad de Ingeniería, Universidad Nacional de La Plata (UNLP), 47 y 116, B1900AJJ, La Plata, Bs. Aires, Argentina

ARTICLE INFO

Article history:

Received 28 December 2010

Received in revised form

11 November 2011

Accepted 22 November 2011

Published online 14 December 2011

The anaerobic degradation of particulate-containing potato processing wastewater using a mixed culture from an industrial anaerobic wastewater treatment plant as inoculum was characterised and modelled. Anaerobic digestion is being increasingly used for wastewater treatment, particularly those which contain high levels of biodegradable matter such as potato processing effluents. A major prerequisite for its proper modelling is a reliable wastewater characterisation with a proper discrimination of the chemical oxygen demand (COD) fractions. These wastewaters contain both soluble (S) and particulate (X) organic load that are assimilated by microorganisms at different rates. Furthermore, these wastewaters generally contain both solid (X_i) and soluble (S_i) inert to anaerobic degradation fractions. In this work, a procedure to determine the COD fractions of potato wastewater is developed. For the wastewater studied, the initial fraction of inert particulate organic matter (x_{X_i}) was negligible, while the initial fraction of inert soluble organic matter (x_{S_i}) was $20.94\% \pm 1.65$. A model with first-order serial-parallel reactions system was developed for biodegradable fractions. This model has demonstrated its capability to predict the behaviour of the system and can be used for further research work or more complex reactor design.

© 2011 IAGrE. Published by Elsevier Ltd. All rights reserved.

1. Introduction

During anaerobic digestion, organic material is biologically converted to a variety of end products including biogas, whose main components are methane (65–70%) and carbon dioxide (25–35%) (Olthof & Oleszkiewick, 1982). The advantages and disadvantages of anaerobic and aerobic treatments have been summarised in previous works (Chan, Chong, Law, & Hassell, 2009). Some of the advantages of the anaerobic process are a low sludge yield, and a high efficiency in the production of methane. The latter can be used as an energy source for

heating or to generate electricity. In contrast to the aerobic waste treatment, which consumes energy significantly, anaerobic digestion processes result in a net reduction in CO₂ emissions (Siles, Martín, Chica, & Borja, 2008); moreover the sludge production from an anaerobic process is about five times less than that produced by an aerobic process (Nishio & Nakashimada, 2007). However, anaerobic treatment is much slower than aerobic and usually requires a larger reactor volume. Although anaerobic digestion processes have been conducted for decades, interest in the recovery of methane gas from industrial and agricultural wastewaters has recently

* Corresponding author. Tel.: +54 223 481 6600x261; fax: +54 223 481 0046.

E-mail addresses: durruty@fi.mdp.edu.ar (I. Durruty), zaritzky@ing.unlp.edu.ar (N.E. Zaritzky), froilan@fi.mdp.edu.ar (J.F. González).
1537-5110/\$ – see front matter © 2011 IAGrE. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.biosystemseng.2011.11.012

Nomenclature			
Ac^-	acetate concentration (mol $[Ac^-]l^{-1}$)	X_I	particulate inert COD fraction (mg $[O_2]l^{-1}$)
Ac'	acetate concentration expressed as equivalent COD (mg $[O_2]l^{-1}$)	X_P	particulate product COD fraction, biomass (mg $[O_2]l^{-1}$)
k_1	specific kinetic coefficient for degradation of biodegradable particulate matter (l $mg^{-1} [O_2]d^{-1}$)	$Y_{AC/SB}$	soluble biodegradable matter to acetate dimensionless yield coefficient
k_2	specific kinetic coefficient for degradation of soluble particulate matter (l $mg^{-1} [O_2]d^{-1}$)	$Y_{AC/XB}$	particulate biodegradable matter to acetate dimensionless yield coefficient
k_1^{app}	apparent first-order kinetic coefficient for degradation of X_B (d^{-1})	Y_H	particulate biodegradable to soluble biodegradable yield coefficient or hydrolysis yield coefficient
k_2^{app}	apparent first-order kinetic coefficient for degradation of S_B (d^{-1})	$Y'_{M/AC}$	acetate to methane by acetoclastic bacteria dimensionless yield coefficient
M	methane volume (ml)	$Y'_{M/SB}$	soluble biodegradable matter to methane by hydrogenotropic bacteria dimensionless yield coefficient
M'	methane volume per unit of reaction volume expressed as equivalent COD (mg $[O_2]l^{-1}$)	Y'_{M1}	global yield coefficient that represents the contribution on methane production of particulate degradation via acetoclastic pathway ($Y'_{M1} = Y'_{AC/XB} \cdot Y'_{M/AC}$)
S_B	soluble biodegradable COD fraction (mg $[O_2]l^{-1}$)	Y'_{M2}	global yield coefficient that represents the contribution on methane production of soluble biodegradable degradation via acetoclastic and hydrogenotropic pathways ($Y'_{M2} = Y'_{AC/SB} \cdot Y'_{M/AC} + Y'_{M/SB}$)
$S_{degraded}$	soluble biodegradable COD degraded at any time t_i (mg $[O_2]l^{-1}$)	$Y_{Sp/SB}$	soluble biodegradable matter to soluble metabolic products yield coefficient
S_I	soluble inert COD fraction (mg $[O_2]l^{-1}$)	$Y_{Sp/XB}$	global particulate biodegradable matter to soluble metabolic products yield coefficient
S_P	soluble metabolic product COD fraction (mg $[O_2]l^{-1}$)	$Y_{Xp/SB}$	soluble biodegradable matter to particulate products yield coefficient
t	time (d)	$Y_{Xp/XB}$	global particulate biodegradable matter to particulate products yield coefficient
V	reaction volume (l)		
X_{SB}	ratio between initial biodegradable soluble fraction and the initial total organic load		
X_{SI}	ratio between inert soluble fraction and the initial total organic load		
X_{XB}	ratio between initial biodegradable particulate fraction and the initial total organic load		
X_{XI}	ratio between inert particulate fraction and the initial total organic load		
X_{XP}	ratio between initial particulate product (inoculum) and the initial total organic load		
X_B	particulate biodegradable COD fraction (mg $[O_2]l^{-1}$)		
$X_{degraded}$	particulate biodegradable COD degraded at any time t_i (mg $[O_2]l^{-1}$)		
		<i>Subscript</i>	
		A, B, C, D	relative to batches A, B, C or D respectively
		0	initial
		i	at time i
		f	final

increased due to changing socio-economic situations (Nishio & Nakashimada, 2007). Also, biological treatment appears to be a promising technology to attain revenue from certified emission reduction (CER) credits, more commonly known as carbon credits from the clean development mechanism (CDM) since methane gas generated from anaerobic digestion can be utilised as renewable energy (Chan et al., 2009).

Potato production in Argentina is concentrated mainly in the southeast of the province of Buenos Aires. Between 300 and 400 thousand tonnes of potatoes per year are used for industrial processing, generating large amounts of wastewater, composed mainly of water washing and peeling and chipping debris. Currently, these wastes are subject to biological digestion, both aerobic (Lasik, Nowak, Krzywonos, & Cibis, 2010) and anaerobic (Parawira, Murto, Zvauya, & Mattiasson, 2004) to reduce the organic pollution load.

Sound kinetic modelling of the anaerobic degradation of complex wastes is increasingly needed for a better understanding of the performance of these systems (García-Ochoa,

Santos, Naval, Guardiola, & López, 1999). A major prerequisite for modelling is a reliable wastewater characterisation with COD fractionation, for the identification of organics with different biodegradability properties in order to provide the necessary experimental support to the model (Orhon, Karahan, & Sözen, 1999).

Industrial potato wastewaters contain soluble and particulate organic load (Sentürk, Ince, & Onkal Engin, 2009), mainly starch and soluble carbohydrates, that are assimilated by anaerobic microorganisms at different rates. It is very common to find nutrient deficiencies, so any nutritional supplementation could affect the degradation of pollutants. Due to the ease of digestion of starch by bacteria, rates of anaerobic degradation and methane production are usually faster than in cellulosic materials, considered the most abundant biomass resource (Nishio & Nakashimada, 2007). Furthermore, wastewaters generally contain an inert solid or soluble organic fraction (Orhon et al., 1999). In addition, the different stages in the process have different associated yield coefficients (Blanch & Clark, 1996).

The goals of our approach to the modelling of anaerobic degradation of particulate-containing wastewater were: a) to develop a procedure to estimate the fractions of the COD loads that are refractory to anaerobic biodegradation based on knowledge of characterisation and aerobic degradation of domestic and industrial wastewater; b) to characterise COD fractions of potato wastewater and to determinate the yield coefficients for each step, adapting to anaerobic conditions the Orhon method (Orhon, Artan, & Ate, 1994); c) to evaluate the evolution of biodegradable soluble and particulate COD fractions during the anaerobic degradation of the wastewater by a mixed culture, d) to develop a non-structured kinetic model for anaerobic digestion of potato wastewater capable of describing the changes in the different COD organic fractions and methane production e) to estimate the kinetic parameters by fitting the experimental data of biodegradable COD fractions obtained in a batch treatment.

2. Model description

The total COD (TCOD) of the wastewater can be divided into a refractory or inert (*I*) organic fraction and a biodegradable (*B*) organic fraction. Only the *B* fraction undergoes transformations during the anaerobic biological process, while the *I* fraction is defined as the fraction that is not affected by anaerobic treatment. Both fractions, the inert and the biodegradable, can in turn be split into soluble (*S*) and particulate (*X*) fractions by physical separation such as filtration or centrifugation. Eq. (1) summarises the COD fractionation described above and adopted in this study for potato wastewater undergoing anaerobic degradation. The main reason to

determine the *I* fractions is to evaluate properly the microbial production of residual products, in soluble *S_p* and in particulate *X_p* forms (Boursier, Béline, & Paul, 2005).

$$TCOD = S_I + X_I + S_B + X_B \quad (1)$$

Based on this COD fractionation, Fig. 1 outlines the proposed model. It is assumed that in the first step the particulate biodegradable matter (*X_B*) is degraded to soluble biodegradable matter (*S_B*) and acetate (*Ac⁻*) that is not detectable by COD method (APHA, 1998). The concepts of disintegration, solubilisation, enzymatic hydrolysis and acetogenesis are usually expressed by this general kinetic term of hydrolysis in most of the practical cases presented in the literature (Batstone et al., 2002; Vavilin, Fernandez, Palatsi, & Flotats, 2008). Later, the soluble biodegradable matter (*S_B*) is converted to soluble metabolic products (*S_p*), particulate products, mainly biomass (*X_p*) and methane (*M*). Methanogenesis occurs through three basic biochemical reactions that are controlled by three different groups of methane-forming bacteria (acetoclastic methanogens, hydrogenotrophic methanogens, and methylotrophic methanogens). Acetoclastic methanogens produce methane by “splitting” acetate. Hydrogenotrophic methanogens produce methane by combining hydrogen and carbon dioxide, and methylotrophic methanogens produce methane by removing methyl (–CH₃) groups from simple substrates (Gerardi, 2003). In anaerobic digesters, acetoclastic methane-forming bacteria produce most of the methane, while hydrogenotrophic methane-forming bacteria produce approximately 30% of all methane. Methylotrophic methane-forming bacteria produce a relatively small quantity of methane in anaerobic digesters (Gerardi, 2003). In the model proposed here the acetate produced during hydrolysis is directly converted to

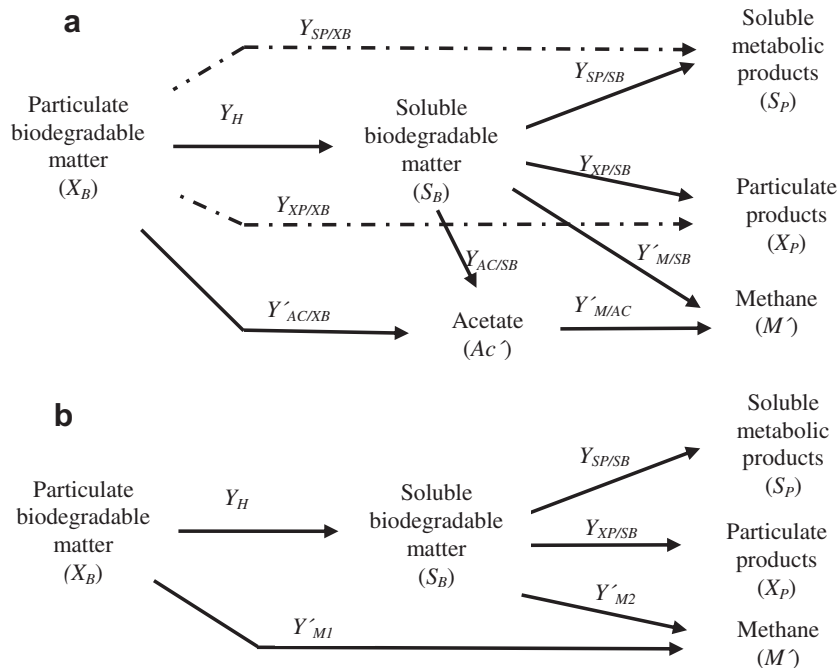


Fig. 1 – Proposed model a) extended model with different compounds and yield coefficients defined in Table 1. b) Simplified model when the methane production is considered as a contribution of particulate degradation via acetoclastic pathway ($Y'_{M1} = Y'_{AC/XB} \cdot Y'_{M/AC}$) and a contribution of soluble biodegradable degradation via acetoclastic and hydrogenotrophic pathways ($Y'_{M2} = Y'_{AC/SB} \cdot Y'_{M/AC} + Y'_{M/SB}$).

methane (M) by acetoclastic methanogenic bacteria. On the other hand part of S_B is converted to acetate and later to methane (M) by acetoclastic methanogenic bacteria and the other part is converted to methane by hydrotrophic methanogens (Fig. 1a). The methylotrophic methanogens contributions was considered negligible in this work due to the nature of the organic load being degraded.

The Petersen matrix (Table 1) summarises the stoichiometry of the reaction system and the corresponding yield coefficients are defined in the Nomenclature. The methane per reactor volume (M') and acetate concentration (Ac') can be expressed as equivalent COD (the amount of O_2 needed to oxidise these to CO_2 and H_2O). Then the dimensionless yield coefficients $Y'_{M/AC}$, $Y'_{AC/SB}$, $Y'_{M/SB}$ and $Y'_{AC/XB}$ can be obtained.

2.1. Kinetic model

Several complete structured kinetic models have been developed for the anaerobic process (Batstone et al., 2002; Batstone, Keller, Newell, & Newland, 2000a) and have been validated in practical applications (Batstone & Keller, 2003; Batstone, Keller, Newell, & Newland, 2000b; Shang, Johnson, & Siegel, 2005). At the cost of increasing complexity, these models are very complete and take into account a set of physico-chemical equations, incorporate gas transfer and ionic reactions and also structured biochemical equations. However, these models consider up to 26 dynamic state concentration variables per reactor vessel or element, and a deep knowledge of the system and intermediate concentrations is needed to apply these models.

Simpler models that study the variation of complex substrates using a global parameters such COD, biological oxygen demand (BOD) or volatile suspended solids (VSS) are more useful in industrial applications where usually the instruments to measure concentrations of intermediates are not available. Several authors proposed complex kinetic models to fit global parameters during anaerobic biodegradation (Beltran, Gonzalez, & Garcia, 2008; Bhunia & Ghangrekar, 2008; Sosnowski, Klepacz-Smolka, Kaczorek, & Ledakowicz, 2008; Vavilin et al., 2008). However, the simplest first-order power law serial-parallel system reaction fits properly in most of the cases (García-Ochoa et al., 1999; Ponsá, Gea, & Sánchez, 2011; Siles et al., 2008).

Based on the model described previously (Fig. 1), a first-order serial-parallel reactions kinetic model is proposed in this work (Table 1). The first-order constant k_1^{app} can be changed to introduce a biomass concentration (X_P) as $k_1 \cdot X_P$ (Vavilin et al., 2008). Then, k_1 and k_2 are specific kinetic constants and k_1^{app} and k_2^{app} are the apparent first-order kinetic constants. Solving the dynamic mass balance for X_B , S_B , X_P and S_P using the yield coefficients detailed in Petersen matrix (Table 1) results in:

$$\frac{dX_B}{dt} = -k_1^{app} \cdot X_B = -k_1 \cdot X_P \cdot X_B \quad (2)$$

$$\frac{dS_B}{dt} = Y_H \cdot k_1^{app} \cdot X_B - k_2^{app} \cdot S_B = Y_H \cdot k_1 \cdot X_P \cdot X_B - k_2 \cdot X_P S_B \quad (3)$$

$$\frac{dX_P}{dt} = Y_{X_P/S_B} k_2^{app} \cdot S_B = Y_{X_P/S_B} k_2 \cdot X_P S_B \quad (4)$$

$$\frac{dS_P}{dt} = Y_{S_P/S_B} k_2^{app} \cdot S_B = Y_{S_P/S_B} k_2 \cdot X_P S_B \quad (5)$$

The methane mass balance is also solved to predict the methane production as:

$$\frac{1}{V} \frac{dM}{dt} = Y_{M/AC} \cdot k_M \cdot X_P \cdot Ac' + Y_{M/SB} k_2 \cdot X_P S_B \quad (6)$$

where M is expressed in ml $[CH_4]$. Or, according with the dimensionless yield coefficients used in Petersen matrix, the differential expression can be expressed as

$$\frac{dM'}{dt} = Y'_{M/AC} \cdot k_M \cdot X_P \cdot Ac' + Y'_{M/SB} k_2 \cdot X_P S_B \quad (7)$$

where M' is expressed as $mg [O_2] l^{-1}$ and it represents the methane as equivalent COD per unit of reaction volume. Since the production of methane from acetate is faster than the previous acetogenic stage (Gerardi, 2003; Vavilin et al., 2008) it can be assumed that the acetate disappears as it is produced. Therefore,

$$k_M \cdot X_P \cdot Ac' = Y'_{AC/XB} \cdot k_1 \cdot X_P \cdot X_B + Y'_{AC/SB} \cdot k_2 \cdot X_P \cdot S_B \quad (8)$$

Substituting Eq. (8) into Eq. (7)

Table 1 – Pettersen matrix for proposed model.

Component Process	X_B (mg $[O_2] l^{-1}$)	S_B (mg $[O_2] l^{-1}$)	X_P (mg $[O_2] l^{-1}$)	S_P (mg $[O_2] l^{-1}$)	Ac' (mg $[O_2] l^{-1}$) ^a	M' (mg $[O_2] l^{-1}$) ^(a)	Reaction rate
Particulate biodegradable organic load degradation	-1	Y_H	-	-	$Y'_{AC/XB}$	-	$k_1 \cdot X_P \cdot X_B$
Soluble biodegradable organic load degradation	-	-1	Y_{X_P/S_B}	Y_{S_P/S_B}	$Y'_{AC/SB}$	$Y'_{M/SB}$	$k_2 \cdot X_P S_B$
Acetate to methane	-	-	-	-	-1	$Y'_{M/AC}$	$k_M \cdot X_P Ac'$

a The volume of methane gas per unit of reactor volume and the acetate concentration was expressed as the O_2 needed to oxidise it to CO_2 and H_2O (COD equivalent) to allow the use of dimensionless yield coefficients.

$$\begin{aligned}
 \frac{dM}{dt} &= Y'_{M/AC} \cdot \left(Y'_{AC/XB} \cdot k_1 \cdot X_P \cdot X_B + Y'_{AC/SB} \cdot k_2 \cdot X_P \cdot S_B \right) + Y'_{M/SB} k_2 \cdot X_P S_B \\
 &= Y'_{M/AC} \cdot Y'_{AC/XB} \cdot k_1 \cdot X_P \cdot X_B + \left(Y'_{AC/SB} \cdot Y'_{M/AC} + Y'_{M/SB} \right) k_2 \cdot X_P S_B \\
 &= Y'_{M1} k_1 \cdot X_P \cdot X_B + Y'_{M2} k_2 \cdot X_P S_B
 \end{aligned} \quad (9)$$

where Y'_{M1} is a global yield coefficient that represents the contribution to the methane production by the particulate degradation via acetoclastic pathway ($Y'_{M1} = Y'_{AC/XB} \cdot Y'_{M/AC}$) and Y'_{M2} is a global yield coefficient that represents the contribution to the methane production by soluble biodegradable degradation via acetoclastic and hydrogenotropic pathways ($Y'_{M2} = Y'_{AC/SB} \cdot Y'_{M/AC} + Y'_{M/SB}$). Fig. 1b represents the simplified model with these global yield coefficients.

2.2. Yield coefficients and inert fraction determination

Previously, the fraction intractable to anaerobic treatment (I) has been estimated as the portion of organic matter that remains at the end of test without discriminating between products and original inert organic matter (Borja, Martín, Banks, Alonso, & Chica, 1995; Ponsá et al., 2011; Vavilin et al., 2008). In this work, a method originally developed by Orhon et al. (1994) to estimate the COD fraction inert to aerobic degradation was adapted to anaerobic conditions. The original method involves three aerated batch runs; two of them are carried out with the wastewater to be studied and the third one with glucose. Other authors (Boursier et al., 2005; Xu, Nakhla, & Patel, 2006) have proposed different modifications to this method in municipal and industrial wastewater, also in aerobic conditions. However, this paper is the first contribution which adapts the Orhon method to make it suitable for anaerobic systems.

In the modified method the characterisation of the COD fraction was carried out using batch tests performed in anaerobic stirred reactors instead of the aerated ones used by

Orhon et al. (1994). Another important modification is that under aerobic conditions the authors distinguished the biodegradable fraction between readily and slowly biodegradation fraction based on respirometric assays and obtained heterotrophic yield coefficients from the same assay. In this work the biodegradable fraction was separated into soluble and particulate fraction by centrifugation and an additional batch experiment was performed with potato starch to estimate the yield coefficients for the anaerobic hydrolysis. Finally, the modified method uses anaerobic yield coefficients instead of the aerobic coefficients reported by Orhon et al. (1994).

In summary, four anaerobic batch tests were needed in this technique to perform a correct characterisation of the COD fractions under anaerobic conditions. The first wastewater reactor (batch A) was started with non-filtered wastewater sample (TCOD), and the second (batch B) with filtered wastewater sample, corresponding to soluble COD (SCOD). The third reactor (batch C) was started with glucose (biodegradable soluble COD) and the fourth reactor (batch D) was started with potato starch (biodegradable solid COD). All the reactors were inoculated with the same amount of anaerobic activated sludge (X_{P0}) at the start-up of degradation. The total and soluble COD were measured at initial (t_0) and at final times (t_f) in each of the reactors. Figure 2 represents the fate of organic fractions in the different batch assays during the characterisation experiments.

COD fractions in batch C were calculated based on total COD (TCOD) and soluble COD (SCOD) measured at the beginning (t_0) and at the end (t_f) of the batch assay.

$$S_{BC} = \text{TCOD}_C(t_0) - X_{P0} \quad (10)$$

$$S_{PC} = \text{SCOD}_C(t_f) \quad (11)$$

$$X_{PC} = \text{TCOD}_C(t_f) - \text{SCOD}_C(t_f) \quad (12)$$

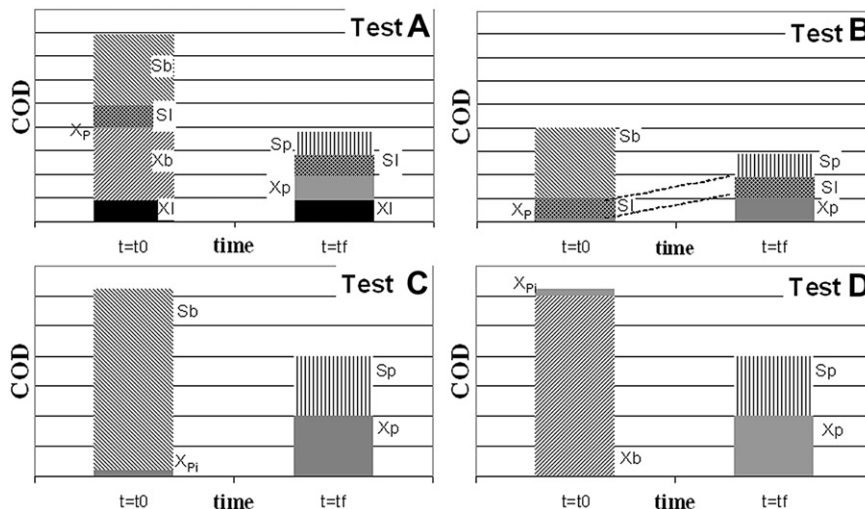


Fig. 2 – Modifications of the organic fractions in the different batch assays during the characterisation test. Batches A and B contained total and soluble wastewater respectively, batch C contained glucose and batch D contained potato starch. S_1 represents the inert soluble organic load and X_l the inert particulate organic load. S_b represents the initial biodegradable soluble organic load and X_b the initial biodegradable particulate organic load; S_p and X_p represent final metabolic soluble products and particulate products, mainly biomass.

The soluble biodegradable matter to soluble metabolic products yield coefficient (Y_{S_p/S_b}) and the soluble biodegradable matter to particulate products yield coefficient (Y_{X_p/S_b}) were estimated as:

$$Y_{S_p/S_b} = \frac{S_{PC}}{S_{BC}} \quad (13)$$

$$Y_{X_p/S_b} = \frac{X_{PC} - X_{P0}}{S_{BC}} \quad (14)$$

Similarly, the global particulate biodegradable matter to soluble metabolic products yield coefficient (Y_{S_p/X_B}) and a global particulate biodegradable matter to particulate products yield coefficient (Y_{X_p/X_B}) have been estimated from batch D. These last coefficients involve the hydrolysis from particulate biodegradable matter (X_B) to soluble biodegradable matter (S_B) followed by the conversion to soluble metabolic products (S_p) and particulate products (X_p).

COD measurement in batch D gives the respective COD fractions.

$$X_{BD} = \text{TCOD}_D(t_0) - X_{P0} \quad (15)$$

$$S_{PD} = \text{SCOD}_D(t_f) \quad (16)$$

$$X_{PD} = \text{TCOD}_D(t_f) - \text{SCOD}_D(t_f) \quad (17)$$

and,

$$Y_{S_p/X_B} = \frac{S_{PD}}{X_{BD}} \quad (18)$$

$$Y_{X_p/X_B} = \frac{X_{PD} - X_{P0}}{X_{BD}} \quad (19)$$

Thus, assuming that the starch is hydrolysed to glucose, Y_H can be estimated using the yield coefficients obtained by Eqs. (13) and (14) as follows:

$$Y_H = \frac{S}{X_{BD}} = \frac{1}{2} \left(\frac{X_{PD}}{Y_{X_p/S_b}} + \frac{S_{PD}}{Y_{S_p/S_b}} \right) \quad (20)$$

where S represents soluble matter obtained from X_{BD} by hydrolysis, which is later degraded to X_{PD} and S_{PD} with the respective yield coefficients. The value for S was calculated as the average between the values obtained from both possible ways of degradation.

The inert organic fraction was estimated from data obtained from batches A and B in a similar way to the procedure used by Orhon et al. (1994). The measurement of COD at the beginning and at the end of each assay led to:

$$\text{TCOD}_A(t_0) - \text{SCOD}_A(t_0) = X_{IA} + X_{BA} + X_{P0} \quad (21)$$

$$\text{SCOD}_A(t_0) = S_{IA} + S_{BA} \quad (22)$$

$$\text{TCOD}_A(t_f) - \text{SCOD}_A(t_f) = X_{IA} + X_{PA} \quad (23)$$

$$\text{SCOD}_A(t_f) = S_{IA} + S_{PA} \quad (24)$$

$$\text{TCOD}_B(t_0) - X_{P0} = \text{SCOD}_B(t_0) = S_{IB} + S_{BB} \quad (25)$$

$$\text{TCOD}_B(t_f) - \text{SCOD}_B(t_f) = X_{PB} \quad (26)$$

$$\text{SCOD}_B(t_f) = S_{IB} + S_{PB} \quad (27)$$

The mass balances for soluble and particulate organic load for each batch, using the yields coefficients defined above are the following:

Batch A

$$\text{Soluble: } S_{PA} = Y_{S_p/S_b} \cdot S_{BA} + Y_{S_p/X_B} \cdot X_{BA} \quad (28)$$

$$\text{Particulate: } X_{PA} = Y_{X_p/S_b} \cdot S_{BA} + Y_{X_p/X_B} \cdot X_{BA} + X_{P0} \quad (29)$$

Batch B

$$\text{Soluble: } S_{PB} = Y_{S_p/S_b} \cdot S_{BB} \quad (30)$$

$$\text{Particulate: } X_{PB} = Y_{X_p/S_b} \cdot S_{BB} + X_{P0} \quad (31)$$

Assuming that the yield coefficients are the same in this wastewater as in the previous case of starch and glucose, the equation system (Eqs. (21)–(24) and (28) and (29)) can be solved, and six unknowns may be estimated (X_{IA} , X_{BA} , S_{IA} , S_{BA} , X_{PA} , S_{PA}). On the other hand, the system of equations (Eqs. (25), (26) and (30)) can be solved to find S_{IB} , S_{BB} , and S_{PB} and also to compare the results obtained before checking the validity of the assumptions. Eqs. (27) and (31) allow the value of Y_{X_p/S_b} to be checked for the wastewater and to compare it with the previously calculated value for glucose.

The initial ratios between each fraction and the total organic load can be expressed for the potato wastewater as:

$$x_{X_I} = 100 \cdot X_I / \text{TCOD}(t_0) \quad (32)$$

$$x_{S_I} = 100 \cdot S_I / \text{TCOD}(t_0) \quad (33)$$

$$x_{X_B} = 100 \cdot X_B(t_0) / \text{TCOD}(t_0) \quad (34)$$

$$x_{S_B} = 100 \cdot S_B(t_0) / \text{TCOD}(t_0) \quad (35)$$

2.3. Temporal evolution of the organic fractions

With the data obtained from the characterisation assay, as described in section 2.2, it was possible to calculate the temporal trends of different organic fractions (X_B , X_p , S_B , S_p) during the batch test in order to fit properly the proposed model. Therefore, the mass balance between the start of the process and a given time t_i , considering that total and soluble COD are known, was solved by:

$$\text{TCOD}(t_i) - \text{SCOD}(t_i) = X_I + X_{Bi} + X_{Pi} \quad (36)$$

$$\text{SCOD}(t_i) = S_I + S_{Bi} + S_{Pi} \quad (37)$$

$$X_{Bi} = X_{B0} - X_{\text{degraded}} \quad (38)$$

$$S_{Bi} = S_{B0} + Y_H \cdot X_{\text{degraded}} - S_{\text{degraded}} \quad (39)$$

$$X_{Pi} = Y_{X_p/X_B} \cdot S_{\text{degraded}} + X_{P0} \quad (40)$$

$$S_{Pi} = Y_{S_p/X_B} \cdot S_{\text{degraded}} \quad (41)$$

It can be noted that, knowing the initial organic fraction, both inert and biodegradable, the six unknown variables (X_{Bi} , X_{Pi} , S_{Bi} , S_{Pi} , $X_{degraded}$, $S_{degraded}$) can be estimated after solving the system of Eqs. (36) to (41) at any time t_i .

3. Materials and methods

3.1. Simulated wastewater

The simulated wastewater was prepared by grinding whole fresh potatoes and adding distilled water in a ratio of 1 l of water to 100 g of fresh potatoes. The resulting suspension was filtered by vacuum through a sieve (mesh size 20 μ m). The addition of water took place in successive leaching stages and washing of cake. Finally peptone was added to ensure the nutrient requirement of COD/N/P ratio 200/5/1 (Krishnan, Ahmad, & Jeru, 2008).

3.2. Inoculum

Activated sludge from a methanogenic industrial digester was used as inoculum. It was kindly supplied by McKein SA (Balcance, Argentina), from its anaerobic wastewater treatment plant.

3.3. Batch test

The characterisation tests (batches A, B, C and D) were carried out in 250 ml Erlenmeyer flasks with constant stirring at 35 °C; samples were taken at the start and at 90 days of degradation. Simultaneously, the wastewater was treated in a batch reactor of 1.5 l with controlled temperature (35 °C) and agitation (200 RPM). Samples were taken at regular intervals until the depletion of the wastewater. The 10% v/v of inoculum was used in all cases ($X_{P0} = 310 \text{ mg } [O_2] l^{-1}$). All the tests were performed in duplicate.

3.4. Analytical methods

The COD was determined using method 5520 (Closed Reflux Method) (APHA, 1998). Samples of 2 ml each were centrifuged for 10 min at 9000g. 1 ml of supernatant was taken for determination of soluble COD. The total COD was measured using non-centrifuged samples after being homogenised in a Wheaton homogeniser and then diluted in distilled water.

3.5. Estimation of the parameters

The kinetic coefficients k_1 and k_2 were obtained by fitting the data of the organic fractions calculated as described in section 2.3 by the least squares method (OriginPro, v 8.0724; OriginLab Corporation, Northampton, MA 01060, USA). The yield coefficients calculated as described in section 2.2 were used. The global yield coefficients Y'_{M1} and Y'_{M2} were calculated from experimental batch data. Once the kinetic parameters were obtained, the concentration profile was modelled solving Eqs. (2)–(5) and Eq. (9) using a fourth-order Runge–Kutta algorithm coupled to the regression in order to integrate the equations simultaneously (Mathcad, version 14.0.0.163; Parametric

Technology Corporation, Needham, MA 02494, USA). The model predictions were verified using one-way analysis of variance (ANOVA) test with a significance level of 0.05 (OriginPro, v 8.0724; OriginLab Corporation, Northampton, MA 01060, USA).

4. Results and discussion

Table 2 shows the yield coefficients obtained from C and D batches applying Eqs. (13), (14), and (18)–(20). The global yield coefficients $Y_{Sp/Xp}$ and $Y_{Xp/Xb}$ were lower than the soluble yield coefficients $Y_{Sp/Sb}$ and $Y_{Xp/Sb}$ because the first pair also included the hydrolysis yield coefficients. Boursier et al. (2005) estimated a theoretical value for the fraction of biodegradable COD converted into particulate products reporting $Y_{Xp} = 0.134$ based on literature data (Henze, Gujer, Mino, & Van Loosdrecht, 2000). This parameter includes both $Y_{Xp/Sb}$ and $Y_{Xp/Xb}$ shown in Table 2. The $Y_{Xp/Sb}$ value obtained in the present work was similar to the theoretical value, and $Y_{Xp/Xb}$ was of the same order of magnitude.

In this work a value of 0.62 was found for Y_H . Since the model considers no production of biomass or product during hydrolysis it was expected that all particulate COD hydrolysed would be converted to soluble COD. However, since general kinetic terms of hydrolysis is a complex term that includes concepts of disintegration, solubilisation, enzymatic hydrolysis and acetogenesis (Batstone et al., 2002; Vavilin et al., 2008) lower yield coefficients could be expected. In addition, due to the limitation of the COD determination test (APHA, 1998), the acetate produced during particulate degradation was not measured as S_b . For this reason the particulate matter to acetate dimensionless yield coefficient, $Y'_{AC/XB}$ was independently determined as 0.17 (see the discussion on methane formation below). On the other hand, not all particulate COD is necessarily converted to soluble exocellular COD. The hydrolytic bacteria could use part of the organic matter as fuel

Table 2 – List of parameters.

Parameter	Value
X_{XI}	0.50% \pm 0.20
X_{SI}	20.94% \pm 1.65
X_{XP}	1.96% \pm 0.20
X_{XB}	62.34% \pm 0.40
X_{SB}	14.25% \pm 3.15
k_1	$1.503 \times 10^{-3} \text{ l mg}^{-1} [O_2] \text{ d}^{-1}$
k_2	$3.865 \times 10^{-5} \text{ l mg}^{-1} [O_2] \text{ d}^{-1}$
$k_1^{aPP} (t=0)$	0.466 d^{-1}
$k_2^{bPP} (t=0)$	0.023 d^{-1}
Y_H	0.616 \pm 0.023
$Y'_{AC/XB}$	0.170 \pm 0.021
$Y'_{AC/SB}$	N/D
$Y'_{M/AC}$	0.667
$Y'_{M/SB}$	N/D
$Y_{Sp/Sb}$	0.034 \pm 0.007
$Y_{Xp/Sb}$	0.133 \pm 0.009
Y'_{M1}	0.114 \pm 0.014
Y'_{M2}	0.345 \pm 0.017
$Y_{Sp/Xp}$	0.021 \pm 0.009
$Y_{Xp/Xb}$	0.082 \pm 0.012

for its metabolic requirements (Bailey & Ollis, 1986). During this step, the hydrolysis and the consumption of hydrolysed matter should be intracellular so the intermediate soluble matter was not measured as soluble COD in the liquid bulk. Values of hydrolysis yield coefficients can be found for anaerobic process (Vavilin et al., 2008), however this parameter is usually expressed as COD consumed converted to volatile fatty acids (VFA) (Sentürk et al., 2009; Sosnowski et al., 2008) or other intermediates (Aldin, 2010; Batstone et al., 2002).

Table 2 shows the initial ratio between each fraction and the total organic load of the potato wastewater calculated by Eqs. (32)–(35) after solving the system of Eqs. (21)–(31). The values obtained in batch A and B differ in less than 5% (in average). The value of the yield coefficient Y_{X_P/S_B} for the wastewater obtained from test B is very close to that obtained for potato starch as substrate. This result validates the assumption detailed in section 2.2.

Vavilin et al. (2008) summarised a range of inert fraction during anaerobic process from 18% (food waste) to 78% (cellulosic waste) and Ponsá et al. (2011) found the inert fraction of anaerobic process for municipal wastewater to vary between 37 and 56%. On the other hand, Orhon, Ates, Sözen, and Çokgör (1997) found an average value of x_{S_i} was 3.6% for domestic wastewater under aerobic conditions and Xu et al. (2006) found x_{S_i} ranging between 3.3% and 5.8% for different tomato-processing wastewaters calculated as in this work. In the present work the value obtained for initial percentage of S_i (x_{S_i}) during anaerobic digestion was 20.94%, which is similar to that reported by Vavilin et al. (2008) for food wastewater but is lower than those reported by Ponsá et al. (2011). However, in this latter study, metabolic products were included in the calculations as an inert fraction. The values reported in this work are higher than those reported for aerobic degradation. This agrees with the observation of Chan et al. (2009) who reported that the effluent quality from an aerobic system is generally higher than the anaerobic system. The initial percentage of X_i (x_{X_i}) found in the present work was 0.5% and could be considered negligible. This value is lower than the reported by Orhon et al. (1997), which ranged from 10% to 29% for municipal wastewaters, and between 37% and 72% for piggery wastewaters (Boursier et al., 2005). These organic fractions, are quite site-specific as evidenced by the data presented by Orhon et al. (1997) and should be experimentally verified for each system under study.

Fig. 3 shows the evolution of different organic load fractions at the beginning and at the end of the test A. Fig. 3 shows that although 31% of the initial organic load remained at the end of the test, only 21% corresponded to the inert fraction and the rest is due to the generation of metabolic products; 28% of the final organic load corresponded to particulate metabolic products (mainly biomass) and 6% to soluble metabolic products; 66% of the final organic load corresponded to inert load (mainly soluble).

The trends for total, solid and soluble COD are shown in Fig. 4. There is a marked decrease in the solid COD and an increase in the COD of soluble compounds during the first 5 days of reaction. These results are related to the decomposition of biodegradable particulate matter, mainly starch, to simpler organic soluble compounds. The composition of the solid fraction also changed as the degradation proceeded. At

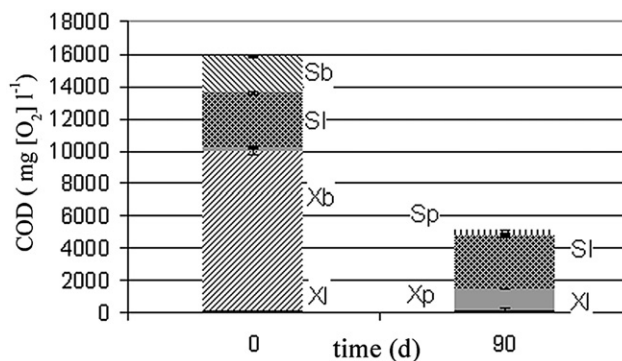


Fig. 3 – Trend of the different organic load fractions at the beginning and at the end of the test A.

the beginning of the test ($t = 0$ d) the solids accumulated in the tubes after centrifugation was white (i.e. starch) with a thin layer of black solid (X_{P0}). The wastewater before inoculation presented only a white sediment. After three days the white fraction was reduced and the black fraction was more notorious; finally after 10 d the white solid disappeared.

Figure 5 shows the modification of the different organics loads (X_B , X_P , S_B , S_P , X_i , S_i) calculated as described in section 2.3 using the equation system Eqs. (36)–(41). The X_B calculated decreased during the first 5 days and X_P began to increase according to the empirical observations. Together with the X_B decrease, an increase of S_B was observed, followed by decay, due to self degradation. The accumulation of S_B demonstrates that the degradation of soluble organic load is slower than the degradation of the particulate organic load. This effect is reflected in the values obtained for k_1 and k_2 , which are shown in Table 1; $k_1 = 1.503 \times 10^{-3} \text{ l mg}^{-1} [\text{O}_2] \text{ d}^{-1}$ is two orders of magnitude higher than $k_2 = 3.865 \times 10^{-5} \text{ l mg}^{-1} [\text{O}_2] \text{ d}^{-1}$. Although the rate-limiting step in anaerobic digestion with suspended organic matter is generally considered to be the hydrolysis of solids (Vavilin et al., 2008), in the present work the hydrolysis was not the limiting factor according to Siles et al. (2008) and Neves, Oliveira, and Alves (2006). A direct comparison of the values obtained in this research with those available in the literature is difficult, since no data are

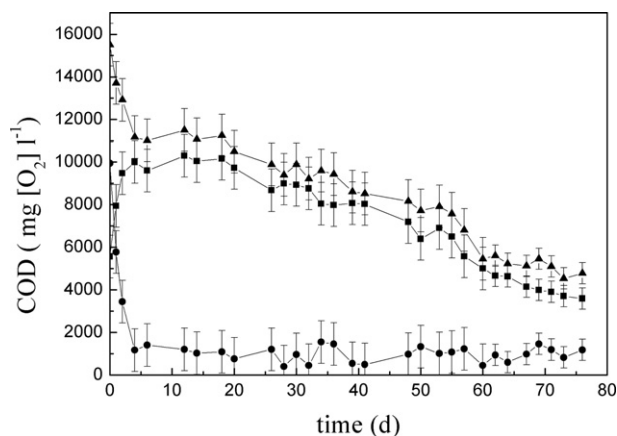


Fig. 4 – Trend of total COD (triangles), soluble COD (squares) and solid COD (circles).

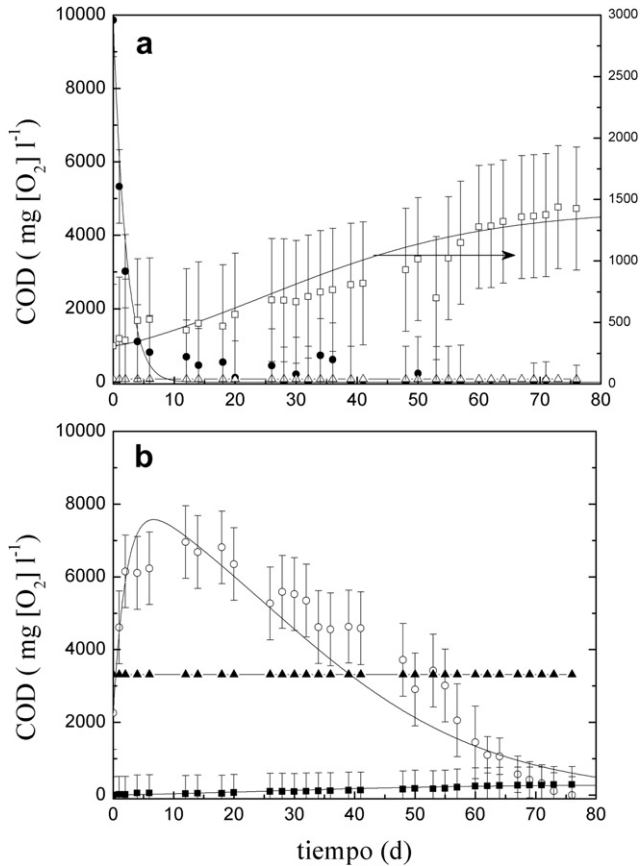


Fig. 5 – Trend of the organic loads calculated as described in section 2.2 using the equation system (dots) versus theoretical values predicted by the model (solid line) a) particulate biodegradable organic load, X_B (filled circles); particulate inert organic load, X_I (open triangles); particulate product organic load, biomass, X_P (open squares) in right axes. b) Soluble biodegradable organic load, S_B (open circles); soluble inert organic load, S_I (filled triangles); and soluble product organic load, S_P (filled squares).

available related to this model for anaerobic potato wastewater treatment. However the value of k_1^{PP} found in the present work is close to the range between 0.2 and 1.08 d^{-1} reported by Boon (1994) for the starch hydrolysis kinetic constants. A wide range of values of the hydrolysis first-order rate coefficient from 0.005 to 2 d^{-1} can be found for composite wastewater and simpler organic materials including carbohydrates, lipids and proteins sources (Neves, Gonçalo, Oliveira, & Alves, 2008; Vavilin et al., 2008). This wide range of values can be explained by different experimental conditions, different hydrolytic biomass to substrate ratios and the lumped effects of disintegration and hydrolysis (Vavilin et al., 2008). In order to distinguish between these effects, the model ADM1 (Batstone et al., 2002) proposes to consider disintegration as a separate hydrolysis processes.

The theoretical values predicted by the model for different organic fractions are also shown in Fig. 5 as solid lines. The experimental methane accumulation and the theoretical values predicted by the proposed model are shown in Fig. 6.

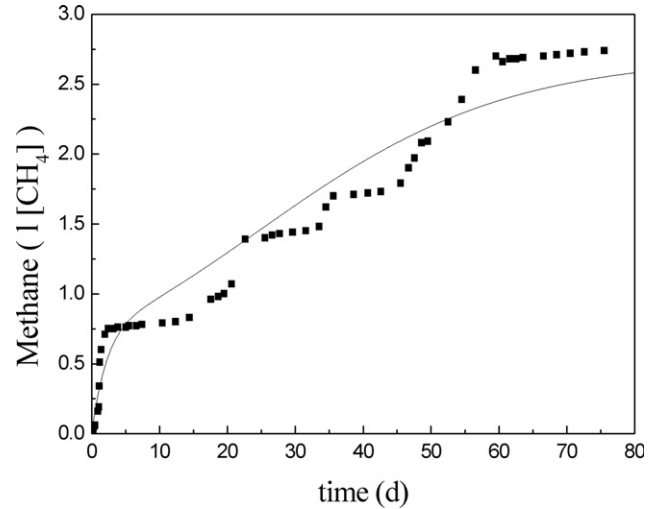


Fig. 6 – Trend of accumulated methane loads, experimental values (dots) and theoretical values predicted by the model (solid line).

The dimensionless global yield coefficient Y'_{M1} was 0.114 (equivalent to $Y_{M1} = 0.045 l [CH_4] g^{-1} [O_2]$). In turn, the dimensionless global yield coefficient Y'_{M2} was 0.345 (equivalent to $Y_{M2} = 0.136 l [CH_4] g^{-1} [O_2]$). These values are in the range reported for methane production yield coefficient (Beltran et al., 2008; Borja et al., 1995; Michaud, Bernet, Buffière, & Delgenès, 2005). The value for $Y_{M/AC}$ was assumed as 1 mol $[CH_4] mol^{-1} [Ac^-]$. The dimensionless $Y'_{M/AC}$ was 0.67 since 3 moles of O_2 are required to oxidise acetate to CO_2 and H_2O , whereas only 2 moles of O_2 are required to oxidise CH_4 to CO_2 and H_2O . Based on the Y'_{M1} definition (Eq. (9)) $Y'_{AC/XB}$ was 0.17. This value is in the range of the previous reported values (Sosnowski et al., 2008; Vavilin et al., 2008). The values of $Y'_{AC/SB}$ and $Y'_{M/SB}$ were not determined in this work. The proper estimation of these parameters requires complete knowledge of the intermediate concentrations involving both acetoclastic and hydrogenotrophic pathways. Further experiments are needed to estimate these values.

Figures 5 and 6 show how the model fits the experimental values. The ANOVA test showed that at the 0.05 significance level the population means were not significantly different in all the cases. This model together with appropriate characterisation can be applied to full-scale anaerobic reactor design and optimisation. This work provides a useful tool in industrial application since a complex anaerobic degradation of potato wastewater can be modelled based on a easily measured global parameter such a COD.

5. Conclusions

A method to discriminate between the inert and biodegradable fractions of the COD present in the anaerobic treatment of potato processing wastewater has been developed. Each of these, both solid and soluble fractions, were also estimated. The kinetic parameters and the anaerobic yield coefficients were estimated based on these fractions and according with the proposed model. The characterisation data and yield

coefficients obtained in this work together with kinetic parameters are useful to model the anaerobic degradation process based on global parameters that are easy to measure, such a COD. This model has demonstrated its capability to predict the behaviour of the system and can be used for further research work or more complex reactor designs.

Acknowledgements

The support provided by grants from the National University of Mar del Plata (15/G247) and the ANPCyT (PICT N 00556) is gratefully acknowledged. I. Durruty and N.E. Zartizky are associated to CONICET, Argentina.

REFERENCES

- Aldin, S. (2010). *The effect of particle size on hydrolysis and modeling of anaerobic digestion*. London, Ontario, Canada: The University of Western Ontario.
- APHA. (1998). *Standard methods for the examination of water and wastewater* (20th ed.). Washington, DC, USA: American Public Health Association/American Water Works Association/Water Environment Federation.
- Bailey, J., & Ollis, D. (1986). *Biochemical engineering fundamentals*. McGraw-Hill Education.
- Batstone, D. J., & Keller, J. (2003). Industrial applications of the IWA anaerobic digestion model no. 1 (ADM1). *Water Science and Technology*, 47(12), 199–206.
- Batstone, D. J., Keller, J., Angelidaki, I., Kalyuzhnyi, S. V., Pavlostathis, S. G., Rozzi, A., et al. (2002). The IWA anaerobic digestion model no 1 (ADM1). *Water Science and Technology*, 45(10), 65–73.
- Batstone, D. J., Keller, J., Newell, R. B., & Newland, M. (2000a). Modelling anaerobic degradation of complex wastewater. I: model development. *Bioresource Technology*, 75(1), 67–74.
- Batstone, D. J., Keller, J., Newell, R. B., & Newland, M. (2000b). Modelling anaerobic degradation of complex wastewater. II: parameter estimation and validation using slaughterhouse effluent. *Bioresource Technology*, 75(1), 75–85.
- Beltran, J., Gonzalez, T., & Garcia, J. (2008). Kinetics of the biodegradation of green table olive wastewaters by aerobic and anaerobic treatments. *Journal of Hazardous Materials*, 154(1–3), 839–845.
- Bhunja, P., & Ghangrekar, M. M. (2008). Analysis, evaluation, and optimization of kinetic parameters for performance appraisal and design of UASB reactors. *Bioresource Technology*, 99(7), 2132–2140.
- Blanch, H. W., & Clark, D. S. (1996). *Biochemical engineering*. New York: Marcel Dekker Inc.
- Boon, F. (1994). *Influence of pH, high volatile fatty acids concentrations and partial hydrogen pressure on hydrolysis*. Wageningen University.
- Borja, R., Martín, A., Banks, C. J., Alonso, V., & Chica, A. (1995). A kinetic study of anaerobic digestion of olive mill wastewater at mesophilic and thermophilic temperatures. *Environmental Pollution*, 88(1), 13–18.
- Boursier, H., Béline, F., & Paul, E. (2005). Piggery wastewater characterisation for biological nitrogen removal process design. *Bioresource Technology*, 96(3), 351–358.
- Chan, Y. J., Chong, M. F., Law, C. L., & Hassell, D. G. (2009). A review on anaerobic–aerobic treatment of industrial and municipal wastewater. *Chemical Engineering Journal*, 155(1–2), 1–18.
- García-Ochoa, F., Santos, V. E., Naval, L., Guardiola, E., & López, B. (1999). Kinetic model for anaerobic digestion of livestock manure. *Enzyme and Microbial Technology*, 25(1–2), 55–60.
- Gerardi, M. H. (2003). *The microbiology of anaerobic digesters*. New Jersey: John Wiley and Sons.
- Henze, M., Gujer, W., Mino, T., & Van Loosdrecht, M. C. M. (2000). *Activated sludge models ASM1, ASM2, ASM2d and ASM3*, Vol. 9. London: IWA Scientific and Technical Report.
- Krishnan, V., Ahmad, D., & Jeru, J. B. (2008). Influence of COD:N:P ratio on dark greywater treatment using a sequencing batch reactor. *Journal of Chemical Technology and Biotechnology*, 83(5), 756–762.
- Lasik, M., Nowak, J., Krzywonos, M., & Cibis, E. (2010). Impact of batch, repeated-batch (with cell recycle and medium replacement) and continuous processes on the course and efficiency of aerobic thermophilic biodegradation of potato processing wastewater. *Bioresource Technology*, 101(10), 3444–3451.
- Michaud, S., Bernet, N., Buffière, P., & Delgenès, J. P. (2005). Use of the methane yield to indicate the metabolic behaviour of methanogenic biofilms. *Process Biochemistry (Amsterdam, Netherlands)*, 40(8), 2751–2755.
- Neves, L., Gonçalo, E., Oliveira, R., & Alves, M. M. (2008). Influence of composition on the biomethanation potential of restaurant waste at mesophilic temperatures. *Waste Management*, 28, 965–972.
- Neves, L., Oliveira, R., & Alves, M. M. (2006). Anaerobic co-digestion of coffee waste and sewage sludge. *Waste Management*, 26(2), 176–181.
- Nishio, N., & Nakashimada, Y. (2007). Recent development of anaerobic digestion processes for energy recovery from wastes. *The Society for Biotechnology*, 103(2), 105–112.
- Olthof, M., & Oleszkiewicz, J. (1982). Anaerobic treatment of industrial wastewater. *Chemical Engineering*, 15, 1321–1326.
- Orhon, D., Artan, N., & Ate, E. (1994). A description of three methods for the determination of the initial inert particulate chemical oxygen demand of wastewater. *Journal of Chemical Technology & Biotechnology*, 61(1), 73–80.
- Orhon, D., Ates, E., Sözen, S., & Çokgör, E. U. (1997). Characterization and COD fractionation of domestic wastewaters. *Environmental Pollution*, 95(2), 191–204.
- Orhon, D., Karahan, Ö., & Sözen, S. (1999). The effect of residual microbial products on the experimental assessment of the particulate inert COD in wastewaters. *Water Research*, 33(14), 3191–3203.
- Parawira, W., Murto, M., Zvauya, R., & Mattiasson, B. (2004). Anaerobic batch digestion of solid potato waste alone and in combination with sugar beet leaves. *Renewable Energy*, 29, 1811–1823.
- Ponsá, S., Gea, T., & Sánchez, A. (2011). Anaerobic co-digestion of the organic fraction of municipal solid waste with several pure organic co-substrates. *Biosystems Engineering*, 108(4), 352–360.
- Sentürk, E., Ince, M., & Onkal Engin, G. (2009). Treatment efficiency and VFA composition of a thermophilic anaerobic contact reactor treating food industry wastewater. *Journal of Hazardous Materials*, 176(1–3), 843–848.
- 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 Science and Technology*, 52(1–2), 487–492.
- Siles, J. A., Martín, M. A., Chica, A., & Borja, R. (2008). Kinetic modelling of the anaerobic digestion of wastewater derived from the pressing of orange rind produced in orange juice manufacturing. *Chemical Engineering Journal*, 140(1–3), 145–156.
- Sosnowski, P., Klepacz-Smolka, A., Kaczorek, K., & Ledakowicz, S. (2008). Kinetic investigations of methane co-fermentation of sewage sludge and organic fraction of municipal solid wastes. *Bioresource Technology*, 99(13), 5731–5737.

Vavilin, V. A., Fernandez, B., Palatsi, J., & Flotats, X. (2008). Hydrolysis kinetics in anaerobic degradation of particulate organic material: an overview. *Waste Management*, 28(6), 939–951.

Xu, Z., Nakhla, G., & Patel, J. (2006). Characterization and modeling of nutrient-deficient tomato-processing wastewater treatment using an anaerobic/aerobic system. *Chemosphere*, 65(7), 1171–1181.