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Organic fractions influence on biogas generation from potato residues. Kinetic model generalization

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ABSTRACT

Bioenergy production as methane is being increasingly used to process low value by-products or not commercial wastes, in particular those which contain high levels of biodegradable organic matter such as potato residue. This work is a continuation of a previous one, which details the characterization and development of a kinetic model for its biodegradation. The knowledge of the effect of different fed organic fractions on the kinetics allows the development of kinetic models that predict the behavior of the degradation after a fluctuation in the feed characteristics. Information about the influence of each variable over different process stages was found and a generalized model was developed in concordance. It considers: substrate inhibition in the hydrolysis step and uncompetitive inhibition by total organic load in the stage of degradation of the biodegradable soluble material, and the yield of methane. Furthermore, the biomass influence was taken into account on each stage. This generalized model has been successfully able to predict the evolution of the different species throughout the whole range of conditions studied with a single set of parameters.

1. Introduction

During anaerobic digestion the 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%) [1,2]. Thus, the anaerobic digestion presents the advantages of treating influents with high organic concentrations coupled with bioenergy recovery [3]. Furthermore, the high values of chemical energy available in potato starch made the potato residue suitable for energy production by anaerobic digestion [4]. Besides, the use of a residue as raw material to generate energy could presents economical benefits. Also, a possible source of increased revenue available to industries is through taking advantage of the incentives awarded by the Clean Development Mechanism (CDM) under the Kyoto Protocol 1997. Finally, anaerobic digestion appears to be a promising technology to attain revenue from Certified Emission Reduction (CER) credits, more commonly known as carbon credits from the CDM as methane gas is generated and can be utilized as renewable energy [3].

Potato wastes contain both soluble and particulate organic load [5]. A sound kinetic modeling of the anaerobic degradation of complex substrates is increasingly needed for a better understanding of the performance of these systems [6]. A

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Nomenclature

COD	chemical oxygen demand expressed as mg of oxygen divided by liter of solution (mg L^{-1})
k_1	specific kinetic coefficient for degradation of biodegradable particulate matter (L mg^{-1} d^{-1})
k_2	specific kinetic coefficient for degradation of soluble particulate matter (L mg^{-1} d^{-1})
$kmax_1$	maximum specific rate constant for r_1 (generalized model) (mg L^{-1} d^{-1})
$kmax_2$	maximum specific rate constant for r_2 (generalized model) (mg L^{-1} d^{-1}),
K_{I1}	inhibition constant for r_1 (generalized model) (mg L^{-1})
K_{I2}	inhibition constant for r_2 (generalized model) (mg L^{-1})
K_{IM}	inhibition constant for $Y_{M/SB}$ (generalized model) (mg L^{-1})
K_{S1}	half life constant for r_1 (mg L^{-1})
M	methane volume per unit of reaction volume expressed as equivalent COD (mg L^{-1})
m	biomass maintenance coefficient for $Y_{M/SB}$ (generalized model) (L mg^{-1})
n	order which affects x_{xP} in r_2 (generalized model)
r_2	degradation rate of X_B (mg L^{-1} d^{-1})
r_2	net degradation rate of S_B (mg L^{-1} d^{-1})
r_M	methane production rate (mg L^{-1} d^{-1})
r_P	biomass production rate (mg L^{-1} d^{-1})
S_B	soluble biodegradable COD fraction (mg L^{-1})
S_I	soluble inert COD fraction (mg L^{-1})
S_P	soluble metabolic product COD fraction (mg L^{-1})
SCOD	soluble chemical oxygen demand (mg L^{-1})
t	time (d)
TCOD	total chemical oxygen demand (mg L^{-1})
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 L^{-1})
X_I	particulate inert COD fraction (mg L^{-1})
X_P	particulate product COD fraction, biomass (mg L^{-1})
Y	global methane yield coefficient (L_{CH4} g^{-1})
Y_H	particulate biodegradable to soluble biodegradable yield coefficient or hydrolysis yield coefficient
$Y_{M/xB}$	global yield coefficient that represents the contribution on methane production of particulate degradation.
$Y_{M/SB}$	global yield coefficient that represents the contribution on methane production of soluble biodegradable degradation.
$Ymax_M$	maximum yield coefficient (generalized model)
$Y_{SP/SB}$	soluble biodegradable matter to soluble metabolic products yield coefficient
$Y_{xP/SB}$	soluble biodegradable matter to particulate products yield coefficient

major prerequisite for modeling is a reliable fed characterization. This can be achieved with a proper discrimination of the Chemical Oxygen Demand (COD) loads with different biodegradability characteristics. In a previous work Durruty et al. [7] presented a method to characterize the different organic fractions based on a modification of the Orhon method [8]. With this tool, the fractions of biodegradable and inert COD load can be also separated into both soluble and particulate fraction. This discrimination method can be used to evaluate the effect of each organic fraction on the kinetics of degradation.

The presence of particulate matter and its concentration has been shown to influence the kinetics of the degradation process and methane generation [9–11]. However, Parawira et al. [12] highlighted the lack of information on the influence of different operating parameters such as total solid and inoculum substrate ratio on these processes for certain substrates, among which potato wastes are included. Furthermore, research on the effect of organic load or the organic load-inoculum ratio [12–17] has demonstrated that these factors may be efficient tools to improve the process without the addition of any easy-degradable carbon source. Additionally, knowledge of the impact of the organic load on the treatment allows the development of kinetic models that predict the behavior after a fluctuation in the feed flow. This is considered relevant, since the stability against changes in reactor inlet is one of the most important considerations for the design of this kind of process [18].

Kinetic models, whose parameters must be set for each initial condition, have been previously reported in literature [10,19]. These models are useful to study and compare the performance of the process based on the composition. However, they are not so useful in those applications where inlet conditions may vary considerably. Such variability is very common where low value byproducts or residues are used as substrates for energy generation. In the particular case of potato waste its composition depends strongly of variations of the industrial plant operation and the market value of potato starch. Thus, it is very important to develop models that take into account the effect of the feed on the performance of the process, without becoming extremely complex such as the ADM1 model [20]. Inhibitory kinetic models such as the Andrews–Haldane models, Yano, Webbs, Teissier Aiba, etc [21,22] generally have global orders different than one or present exponential relationships. Examples of these models applied to anaerobic systems are found in literature for substrate inhibition [23,24], external inhibitors [23,25] or related to biomass [26].

With the aim to improve the knowledge on bioenergy production as methane, this work introduces a model able to

allow not only prediction of the behavior after a fluctuation in the feeding, but also a preliminary reactor design and process optimization. Thus, the objectives were: a) to study the effects of different organic loads over the energy generation performance; b) to improve the previously presented kinetic model making it able to predict the anaerobic digestion of potato waste under a wide range of feeding conditions.

1.1. Previous kinetic model

In particular, potato waste contain particulate and soluble organic load, mainly in the form of starch and soluble carbohydrates, which are assimilated by anaerobic microorganisms at different rates. As described in Durruty et al. [7] the total COD can be divided into a refractory or inert (*I*) organic fraction and a biodegradable (*B*) organic fraction. Both fractions, the inert and the biodegradable, can in turn be split into soluble (*S*) and particulate (*X*) fractions. Fig. 1 outlines the kinetic model based on this COD fractionation. It is assumed that the particulate biodegradable matter (X_B) is degraded to soluble biodegradable matter (S_B) and acetate that is not detectable by COD method [27]. It can be assumed that the acetate produced during hydrolysis is directly converted to methane (*M*) by acetoclastic methanogenic bacteria [2]. Later, the kinetic model assumes that the metabolic products (S_P), biomass (X_P) and methane (*M*) are produced during the soluble biodegradable matter (S_B) degradation [7].

Thus, a specific first order serial–parallel reactions kinetic model can be used to describe the kinetic behavior. Taking into account the reaction scheme shown in Fig. 1, the particulate biodegradable organic fraction degradation of X_B (r_1) and the net degradation rate of S_B (r_2) are given by:

$$\frac{dX_B}{dt} = (r_1) = -k_1 \cdot X_P \cdot X_B \quad (1)$$

$$\frac{dS_B}{dt} = (r_2) = Y_H \cdot k_1 \cdot X_P \cdot X_B - k_2 \cdot X_P \cdot S_B \quad (2)$$

The biomass production (r_P) can be represented by:

$$\frac{dX_P}{dt} = (r_P) = Y_{XP/SB} \cdot k_2 \cdot X_P \cdot S_B \quad (3)$$

Analogously, S_P and *M* production rate (r_M) can be described as follows:

$$\frac{dS_P}{dt} = Y_{SP/SB} \cdot k_2 \cdot X_P \cdot S_B \quad (4)$$

$$\frac{dM}{dt} = (r_M) = Y_{M/XB} \cdot k_1 \cdot X_P \cdot X_B + Y_{M/SB} \cdot k_2 \cdot X_P \cdot S_B \quad (5)$$

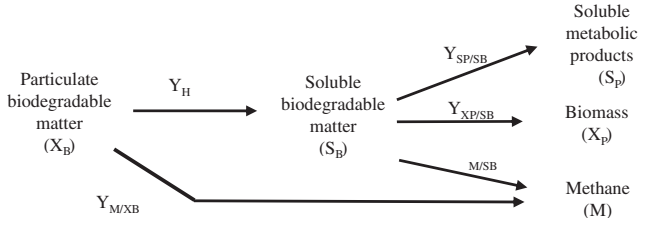

Fig. 1 – Kinetic reaction scheme.

2. Materials and methods

2.1. Substrate and inoculum

The substrate for anaerobic digestion used was a simulated potato residue. It 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 μm). 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. Anaerobic sludge from a working methanogenic industrial digester was used as inoculum. It was kindly supplied by McKein SA (Balcarce, Argentina), from its anaerobic wastewater treatment plant.

2.2. Analytical methods

The COD was determined using method 5520 (Closed Reflux Method) [27]. Samples of 2 ml each were centrifuged for 10 min at 9000 G. 1 ml of supernatant was taken for determination of soluble COD. The total COD was measured using non-centrifuged samples after being homogenized in a Wheaton homogenizer and then diluted in distilled water.

2.3. Experimental procedure

Four batch experiments (I, II, III and IV depicted in Table 1) were conducted at least by duplicate, in a 1.5 L anaerobic reactor with temperature control (35 °C) and agitation (4 s^{-1}). The initial ratio SCOD/TCOD and the total organic load (TCOD) of experiments I, II, III and IV were selected to study the effects of the ratio of soluble/solid organic fractions over the degradation and they are shown on Table 1. Different organic fractions (X_I, X_B, X_P, S_I, S_B) and initial percentages (x_{xI}, x_{xB}, x_{xP}, x_{SI}, x_{SB}) were calculated by the method previously developed by Durruty et al. [7]. The pH was adjusted to 7.2 thorough all the experiments using phosphate-buffer. During the batch tests, samples were taken at regular intervals to monitor pH and composition.

2.4. Kinetic parameter and statistical analysis

The kinetic coefficients k_1 and k_2 were obtained by fitting the data of the organic fractions X_B and S_B, versus time by the least squares method (Origin 8.0, Originlab corporation). The yield coefficients Y_H, $Y_{xP/SB}$, $Y_{SP/SB}$, $Y_{M/xB}$ and $Y_{M/SB}$ were calculated according to the procedure described by Durruty et al. [7]. Furthermore, a parameter Y is defined here as the global methane yield coefficient. The parameters obtained independently for each case are shown in Table 2. The linear regressions and "forward" statistical analysis were performed with R v2.12. (R project). Once the kinetic parameters were obtained, the concentration profile was modeled using a fourth-order Runge–Kutta algorithm coupled to the regression in order to integrate the equations simultaneously (MathCad 14.0.0.163, Parametric Technology Corporation).

Table 1 – Initial wastewater composition in different batch assays.

Exp	TCOD	SCOD	X_B	X_I	S_B	S_I	X_P	x_{XB}	x_{XI}	x_{SB}	x_{SI}	x_{XP}
	mg L^{-1}											
I	2636	2220	18	33	1958	262	364	0.7	1.2	74.3	10.0	14.0
II	4457	3023	1056	68	2832	190	310	23.7	1.6	63.5	4.3	7.0
III	6517	4473	1502	0	4335	138	542	25.1	0.0	72.6	2.2	8.3
IV	6810	2876	3427	47	2569	307	460	50.3	0.6	37.7	4.5	6.8

3. Results and discussion

Table 2 shows the kinetic parameters k_1 and k_2 together with $Y_{M/xB}$, $Y_{M/SB}$ and Y yield coefficients, obtained by independently fitting the model developed by Durruty et al. [7] to the results from the experiments I, II, III and IV. Looking at the data, an inverse relationship can be seen between the organic load and the kinetic constants, what agrees with the results of to Siles et al. [10]. The values of k_1 and k_2 are within the range reported in literature [9,11,17]. In a similar way, the value of the methane yield coefficient obtained falls among those previously reported [28] and lies below the maximum reported by McCarty [29]. The experimental and predicted values are shown as dashed lines on Figs. 2–5 for the experiments I, II, III and IV respectively. In these figures it can be observed how the model developed by Durruty et al. [7] predicts properly the experimental performance. However, it shows better predictions in the early stages of the degradation. This phenomenon is most evident in the experiments with higher initial organic load (III, IV) in which the predicted S_B overestimates the experimental values towards: in the last stages of the degradation and some uncertainty was observed at intermediate times.

3.1. *Linear correlations*

Table 3 shows the linear correlations between different organic fractions. The high value of the regression coefficient indicates a strong correlation between TCOD, $X_{B(t=0)}$ and $S_{I(t=0)}$ and between x_{xI} and x_{xP}. On the other hand there is a very low correlation between $S_{B(t=0)}$ and TCOD and between SCOD, x_{xP} and $X_{I(t=0)}$.

Table 4 shows the linear correlations between organic fractions and the obtained parameters. A negative linear correlation higher than 0.9 for the kinetic constants k_1 and k_2 versus TCOD can be observed. This means that as the total organic load increases the kinetic constants decrease, indicating an inhibitory effect at total organic loads higher than 2500 mg L^{-1}. Results of this kind have not been reported on the anaerobic degradation of potato wastewater. Also, these results are consistent with results previously reported by Siles et al. [10] who observed inhibition by total organic load in the anaerobic degradation kinetics of orange residues for COD loads above 2000 mg L^{-1} in all degradation stages. Also Fang and Yu [15] observed that the anaerobic degradation of gelatin wastewater was impaired by the increased concentration of the organic load at concentrations higher than 2000 mg L^{-1}.

Table 2 – Kinetic parameters and methane yield coefficients in different batch assays.

Exp	k_1	k_2	$Y_{M/xB}$	$Y_{M/SB}$	Y
	L mg^{-1} d^{-1}				L_{CH4} g^{-1}
I	–	2.395×10^{-4}	–	0.305	0.140
II	1.77×10^{-3}	1.008×10^{-4}	0.109	0.125	0.061
III	1.01×10^{-3}	0.9456×10^{-4}	0.096	0.085	0.052
IV	0.29×10^{-3}	0.6785×10^{-4}	0.125	0.015	0.043

The observed values of $Y_{M/xB}$ remained in the order of 0.1 for all the assays, so its linear relationship with the co-variables is not deemed to be relevant. Since Y includes $Y_{M/xB}$ and $Y_{M/SB}$, the high correlation between $Y_{M/SB}$ and Y ($R > 0.98$) is not surprising since $Y_{M/xB}$ can be considered constant. TCOD correlates very well with $Y_{M/SB}$. The sign of the correlation indicates a negative effect on the methane yield as the TCOD increases. This is consistent with previous reports on the anaerobic digestion of wastes from the potato industry with high organic loads [12,13].

Table 4 shows how k_1 has a high linear correlation with X_B with negative sign, indicating substrate inhibition for the hydrolysis step and also with TCOD. However, the rate constant could have an independent correlation with both or, with only one variable and the effect should be translated to the other (due to the high correlation between TCOD and X_B). For this reason the significance must be assessed in a multiple linear regression model. These linear models are widely used for parametric analysis datasets, in biological systems [30] and also in anaerobic digestion systems [31].

To evaluate the degree of mutual significance of the different co-variables in the multiple linear regression models, a "forward" procedure is usually carried out. This method consists on adding one at a time each independent variable to a multiple linear model, beginning with the most significant and evaluating the significance of each added variable in presence of the previously added. The most influential variable on k_1 was X_B followed by TCOD with a low level of significance ($P(F) > 0.23$ in both cases). However, once X_B was included in the model, TCOD lost significance, indicating that the original great significance over k_1 could be attributed to its correlation with X_B (p-value: 0.2296 $R_{adjusted}$: 0.7509).

When the influence over k_2 was studied, the linear regression showed that the most significant variable was the percentage of initial inoculum (x_{xP}) ($P(F) = 0.02138$), analogous to the inoculum to substrate ratio (ISR) reported in literature [12,17]. As the inoculum-substrate ratio increases, k_2 increase. Parawira et al. [12] found that, at 60% of initial inoculum, the

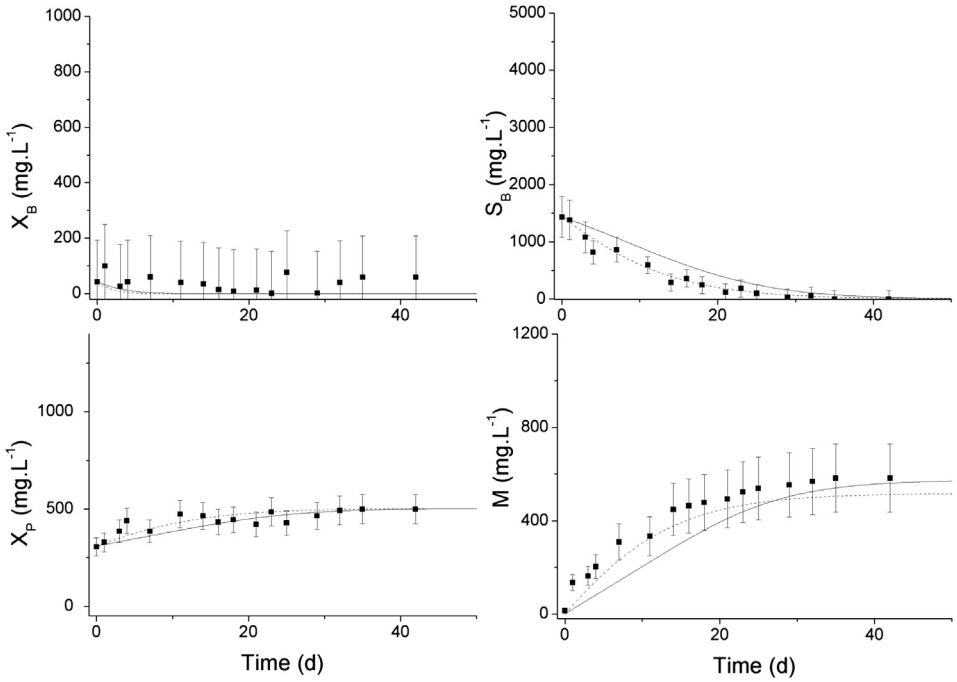

Fig. 2 – Experimental values versus time for assay I. The dashed lines represent the theoretical values predicted by a previous model developed by Durruty et al. [7]. The solid lines represent the theoretical values predicted by the generalized model developed in this work.

potato waste anaerobic degradation performance was optimal. The ratios worked within this work are well below that percentage, so it is expected that an increase in inoculum will result in an improvement in the development process. There is evidence in the literature that inhibition of a biological process depends not only on the substrate concentration of the inhibitor but also on the relationship inoculum to substrate [32,33]. After inclusion of the variable x_{xP} in the model, the next most significant variable was TCOD (P(F) = 0.2464) (*p*-value: 0.0079 $R_{adjusted}$: 0.9998).

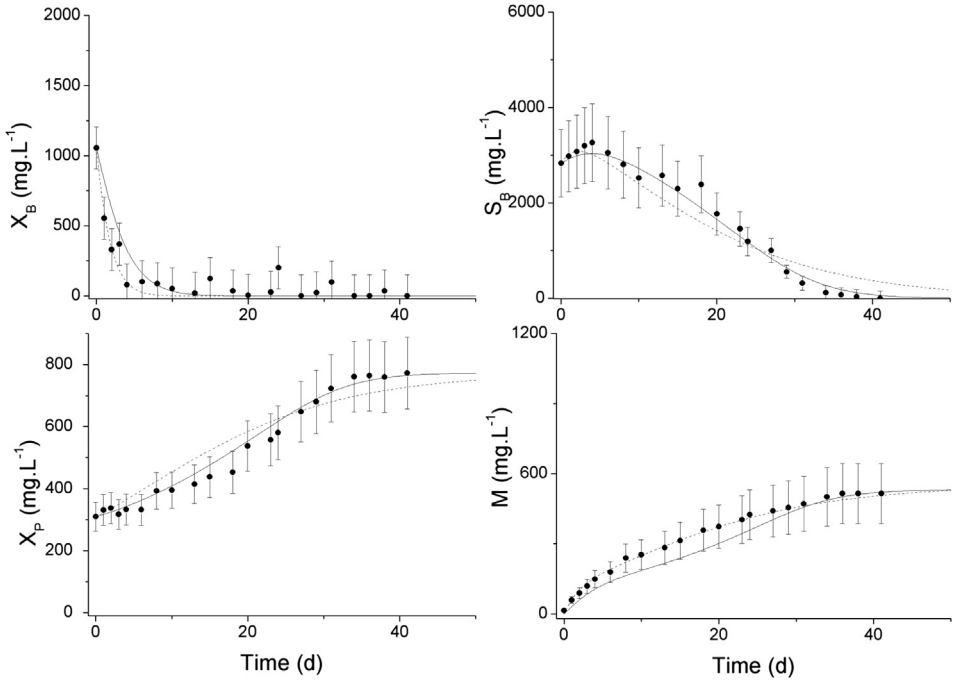

Fig. 3 – Experimental values versus time for assay II. The dashed lines represent the theoretical values predicted by a previous model [7]. The solid lines represent the theoretical values predicted by the generalized model.

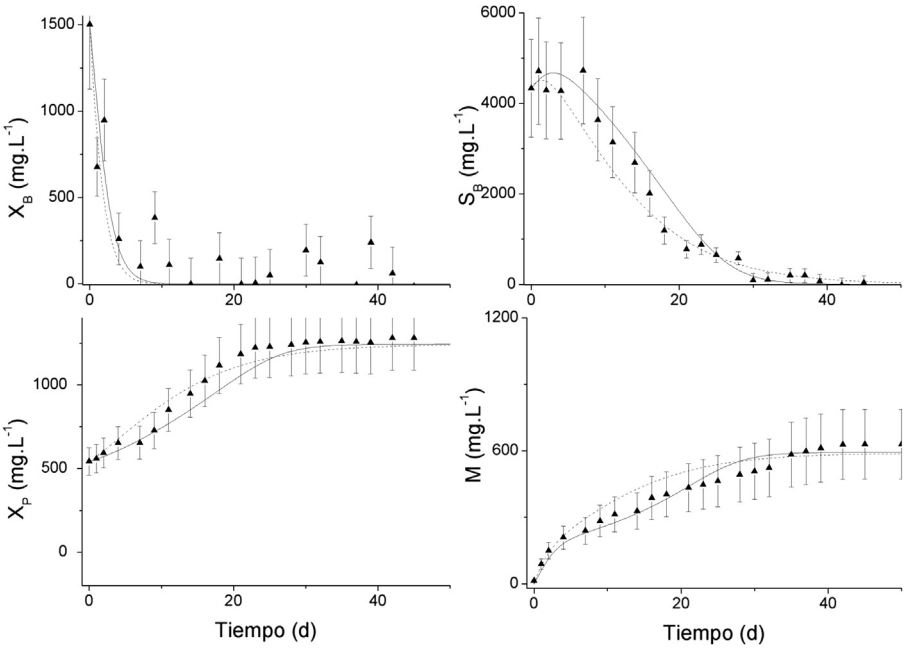

Fig. 4 – Experimental values versus time for assay III. The dashed lines represent the theoretical values predicted by a previous model [7]. The solid lines represent the theoretical values predicted by the generalized model.

In this work, the methane yield is highly correlated with the amount of initial inoculum X_P, which is the most significant variable after adding TCOD to the model (p-value: 0.0003 $R_{adjusted}$: 0.9999). The variable x_{xB} is linearly significant; however by introducing TCOD in the model it lost significance, demonstrating that they are not mutually significant. More biomass generates higher maintenance requirements that generally reduce the yield coefficients of both products and microbial growth [34]. In the case of anaerobic degradation experimental data have shown that the inoculum/substrate ratio affects both the rate and the yield [16]. The increase in methane yield due to the increase in the inoculum size is consistent with the results of Parawira et al. [12] for low percentages.

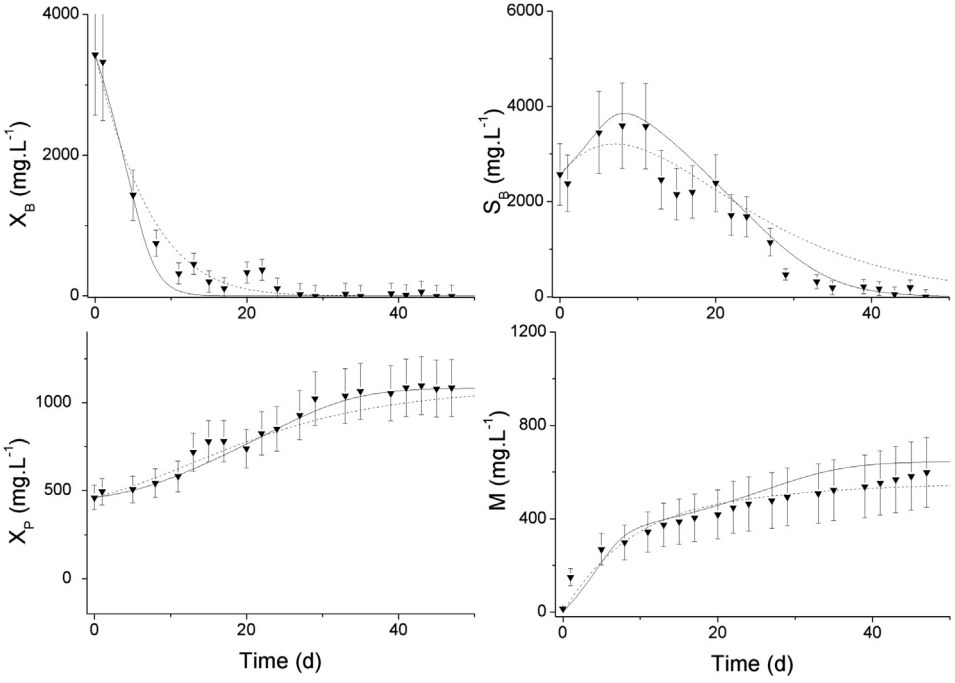

Fig. 5 – Experimental values versus time for assay IV. The dashed lines represent the theoretical values predicted by a previous model [7]. The solid lines represent the theoretical values predicted by the generalized model.

Table 3 – Correlation matrix: organic fractions.

	TCOD	SCOD	X_{B0}	X_{I0}	S_{B0}	S_{I0}	X_{P0}
TCOD	1						
SCOD	0.88673	1					
X_{B0}	0.98445	0.79237	1				
X_{I0}	0.50503	0.17999	0.59859	1			
S_{B0}	−0.10141	0.31624	−0.24360	−0.67173	1		
S_{I0}	0.94016	0.77146	0.94272	0.62740	−0.35966	1	
X_{P0}	−0.23462	0.01183	−0.30547	−0.86984	0.74748	−0.48956	1

3.2. *Non-linear correlations*

Table 5 shows the parameters and the correlation (R^2) to an *n*-th order of different kinetic parameters versus the variables shown to be most significant linear correlations according to the equation:

$$P = A \cdot X^n \tag{6}$$

where *P* is the parameter and *x* the variable.

Table 5 shows that k_1 has a much better fit versus X_B and presents an order of −1.5, which is similar to the global order of Haldane equation which is the most used substrate inhibition kinetic model [24,35]. In turn, k_2 has a low correlation with S_B indicating absence of substrate inhibition at this stage. The order for k_2 versus TCOD close to −1 indicates an inhibition by this variable. Furthermore, the order for X_B is close to zero, what demonstrates independence of this parameter with this variable. While the high order regarding X_{xP} shows a high dependence from this variable.

$Y_{M/xB}$ did not correlate well with any of the different variables. Moreover, the correlation orders close to 0, indicate that $Y_{M/xB}$ remains constant. Similarly, $Y_{M/SB}$ did not show a good correlation with any of the variables. However, the correlations of $Y_{M/SB}$ present high degrees, indicating a high dependence of this parameter from x_{xP} and TCOD fluctuation.

3.3. *Model generalization*

Taking into account the information gathered in Sections 3.1 and 3.2, a generalized model able to predict the degradation behavior for a wide range of varying feed was developed.

Table 4 – Correlation matrix: parameters versus organic fractions.

	k_1	k_2	Y	$Y_{M/xB}$	$Y_{M/SB}$
TCOD	−0.9233	−0.9016	−0.9116	0.1733	−0.9513
SCOD	0.0683	−0.5819	−0.6283	−0.8776	−0.5396
X_{B0}	−0.9357	−0.8143	−0.7954	0.8010	−0.9047
X_{I0}	0.3184	−0.0972	−0.0467	0.6276	−0.0301
S_{B0}	0.1231	−0.5603	−0.6076	−0.9027	−0.5106
S_{I0}	−0.6647	0.1754	0.2235	0.9874	0.04105
X_{P0}	−0.6490	−0.4092	−0.4451	−0.2920	−0.5068
x_{XB}	−0.8815	−0.8944	−0.8757	0.8724	−0.9521
x_{XI}	0.6303	0.3829	0.4200	0.3151	0.4794
x_{SB}	0.7019	0.6229	0.5827	−0.9781	0.7119
x_{SI}	−0.0754	0.9086	0.9305	0.8810	0.8548
x_{XP}	0.0758	0.9786	0.9709	−0.8812	0.9293

As discussed above, the anaerobic degradation of biodegradable particulate material is inhibited by its own substrate. The Andrews–Haldane equation has been applied in most cases of substrate inhibition to enzymatic reactions [21], microbial growth [24,35] or microbial degradation [36]. For this reason, its application in the degradation of particulate biodegradable material is proposed here:

$$r_1 = -\frac{k\,\max_1 \cdot X_B}{K_{S1} + X_B + \frac{X_B^2}{K_{I1}}} \cdot X_P \tag{7}$$

where $k\max_1$ is the maximum specific rate constant, K_{S1} is the half life constant and K_{I1} is the inhibition constant. Equation (7) was adjusted to the experimental data using the least squares method (Origin® 8.0). The $k\max_1$ value resulted 8762.87 L mg^{-1} d^{-1}, $K_{S1}$was 8637.10^6 mg L^{-1} and K_{I1}: 0.369 mg L^{-1} (R^2 adjusted = 0.59). The high value of the half life constant value indicates a low organism-substrate affinity and the low value of the inhibition constant value indicates a strong inhibition due to substrate (X_B).

On the degradation of biodegradable soluble material, the above analysis showed that the variables that affect the degradation rate of biodegradable soluble material in the range studied were: the TCOD (which acts as inhibitor), and the inoculum-substrate ratio, which stimulates it. For this reason the generalized model included this reaction step with a non-competitive inhibition effect by TCOD [21,23] and a positive power law relation respect to x_{xP}, maintaining its first order dependence on SB and the specificity respect to the biomass, X_P:

$$r_2 = -\frac{k\,\max_2 \cdot (x_{XP})^n}{K_{I2} + \mathrm{TCOD}} \cdot S_B \cdot X_P \tag{8}$$

where $k\max_2$ is the maximum specific rate constant, K_{I2} is the inhibition constant and *n* is the order which affects x_{xP}. Fig. 6 shows the fit of the surface versus TCOD and x_{xP} (Origin 8.0® $R^2_{\ \mathrm{adjusted}} = 0.93$). In this figure it can be observed how as the inoculum–substrate ratios increases, the specific rate predicted also increases, while higher TCOD values result in lower rates. The values obtained for the parameters were: $n = 0.304$; $k\max_2 = 0.1458$ L mg^{-1} d^{-1} and $K_{I2} = 32.15$ mg L^{-1}. The small value of K_{I2} indicates moderate inhibition. While the low order regarding the inoculum fraction indicates it does not have a strong influence over the process. The value of *n* is reasonable, since several authors have found a good fit using the half-order model for biomass [26,37]. The proposed model does not consider a maximum for this ratio because experimental data do not present it.

Table 5 – No linear regression to Equation (6).

P	k_1			k_2		
x	A	n	R^2	A	n	R^2
TCOD	6.00×10^8	−3.1606	0.639	2113	−1.1626	0.903
X_B	71.756	−1.5252	0.999	5.00×10^5	−0.2279	0.985
S_B	6.00×10^8	2.3325	0.768	0.180	−0.9603	0.326
x_{XP}	4.00×10^6	2.6148	0.092	4.00×10^6	1.5226	0.905
P	$Y_{M/XB}$			$Y_{M/SB}$		
x	A	n	R^2	A	n	R^2
TCOD	0.062	0.0657	0.0135	6.00×10^7	−2.4141	0.706
X_B	0.035	0.1526	0.4877	1373	−0.4425	0.674
S_B	3867	−0.4425	0.8697	132.7	−0.9285	0.059
x_{XP}	0.960	−1.0896	0.8144	2.00×10^4	2.7941	0.553

The contribution to methane production from both degradative pathways was also considered for the generalized model. $Y_{M/xB}$ was considered constant and equal to the average of the observed data while $Y_{M/SB}$ was affected by X_P and TCOD. The inhibitory effect of the total organic load (TCOD) was taken into account by a non-competitive inhibition kinetics [21] as in the previous case. However, the effect of the concentration of biomass (X_P), was taken into account using a maintenance coefficient [38]. As bacterial populations growth and get old the amount of substrate required for maintenance increases, reducing the availability of nutrients for growth and generate products, what is reflected on their yield coefficients [34]. Then, the equation that describes the evolution of the methane yield coefficient due to degradation of biodegradable soluble material ($Y_{M/SB}$) becomes:

$$Y_{M/SB} = \frac{Y\,max_M}{K_{IM} + TCOD} - m \cdot X_P \tag{9}$$

where $Ymax_M$ is the maximum yield coefficient, K_{IM} is the inhibition constant and m is the biomass maintenance coefficient. Fig. 7 shows the fit of the experimental surface versus TCOD and X_P (Origin 8.0® $R^2_{adjusted} = 0.97$). In this figure it is observed that lower $Y_{M/SB}$ values are predicted as the concentration of biomass increases according to the experimental observations. Furthermore TCOD higher values result in lower yield coefficients due to inhibition. The values obtained for the parameters were: $Ymax_M$ = 441.586 $L.mg^{-1}$; $K_{IM} = 914.12\ mg\ L^{-1}$ and $m = 2.79 \times 10^{-5}\ L.mg^{-1}$. The value of the inhibition constant indicates a substantial inhibition of the methane yield due to total organic load, while a low maintenance coefficient indicates a slightly dependence between $Y_{M/SB}$ and cell maintenance.

To solve the generalized model Equations (7)–(9) were replaced in Equations (1)–(5), resulting in:

$$\frac{dX_B}{dt} = r_1 = -\frac{k\,max_1 \cdot X_B}{K_{S1} + X_B + \frac{X_B^2}{K_{I1}}} \cdot X_P \tag{10}$$

$$\frac{dS_B}{dt} = Y_H \cdot (-r_1) + r_2 = Y_H \cdot \frac{k\,max_1 \cdot X_B}{K_{S1} + X_B + \frac{X_B^2}{K_{I1}}} \cdot X_P - \frac{k\,max_2 \cdot (x_{XP})^n}{K_{I2} + TCOD} \cdot S_B \cdot X_P \tag{11}$$

$$\frac{dX_P}{dt} = Y_{XP/SB} \cdot (r_2) = Y_{XP/SB} \frac{k\,max_2 \cdot (x_{XP})^n}{K_{I2} + TCOD} \cdot S_B \cdot X_P \tag{12}$$

$$\frac{dM}{dt} = Y_{M/XB} \cdot (-r_1) + Y_{M/SB}(TDQO, X_P) \cdot (-r_2) = \overline{Y_{M/XB}} \cdot \frac{k\,max_1 \cdot X_B}{K_{S1} + X_B + \frac{X_B^2}{K_{I1}}} \cdot X_P + \left(\frac{Y\,max_M}{K_{IM} + TCOD} - m \cdot X_P\right) \times \frac{k\,max_2 \cdot (x_{XP})^n}{K_{I2} + TCOD} \cdot S_B \cdot X_P \tag{13}$$

The ordinary differential equations system (10)–(13) was solved using a 4th Order Runge–Kutta routine. The predicted values are shown as solid lines in Figs. 2–5. In these figures it can be seen how the model satisfactorily predicts the behavior

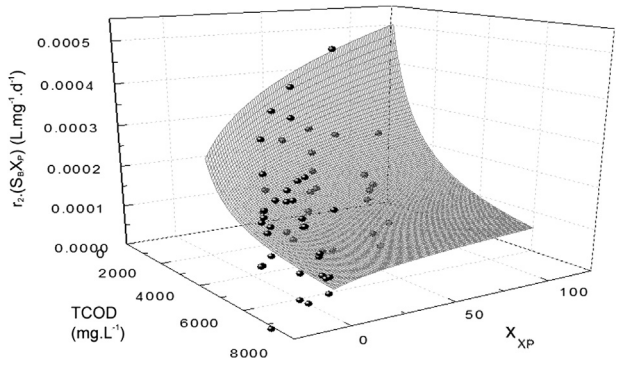

Fig. 6 – Surface fit of Equation (8) to experimental data.

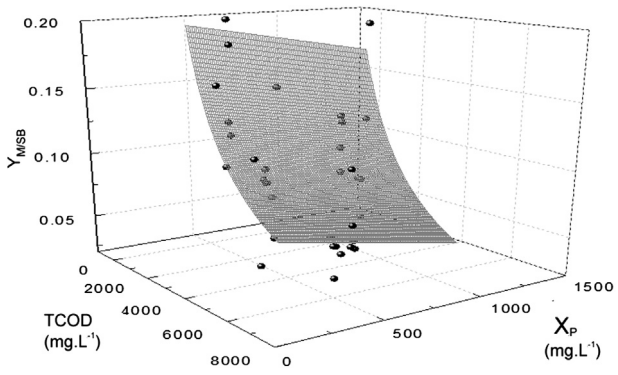

Fig. 7 – Surface fit of Equation (9) to experimental data.

of the all components throughout the whole process. This is more evident at long times where the previous model [7] showed some weakness of fit. In particular, it is relevant the goodness of fit for the degradation of biodegradable soluble material, a critical step of the process. Additionally, the proposed model can successfully predict the behavior of the different compounds for a wide range of feed values.

The generalized model developed in the present work represents a significant improvement with respect to the previously proposed one. From a phenomenological point of view, it considers substrate inhibition in the hydrolysis stage and non-competitive inhibition by total organic load in the step of degradation of biodegradable soluble material and the methane yield. It also takes into account the effect of biomass concentration in those stages. From the operational point of view, the model was able to successfully predict the methane production and the course of the different species in the whole concentration range studied with a single set of parameters.

4. Conclusions

The variable that most affects the process as a whole is the total organic load while the biodegradable particulate organic fraction affects adversely the hydrolysis step. The information obtained allowed to develop a generalized model that considers these effects. This generalized model has been able to predict successfully the behavior of the different species throughout the whole range of conditions studied with single set of parameters. This is important in actual cases where substrates used to generate energy came from several sources and its composition could vary. Thus the model presented here demonstrated to be able to predict the performance of the process as a whole after fluctuations in the feed and it represents a considerable improvement over the previous proposed model.

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