Full Papers

Linearized Kinetic Models for the Simulation of the Mesophilic Anaerobic Digestion of Pre-hydrolyzed Woody Wastes

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The most common kinetic models available in the literature to describe the COD consumption during batch anaerobic digestion are checked and compared in their linearized forms in the case of prehydrolyzed mixtures simulating the composition of woody wastes. The introduction of the COD value at the end of batch digestion in both the First Order and the Monod models allows one to take into account the deviations due to the progressive increase in the fraction of difficultly-digestible substances present in the medium. The so-modified version of the First Order model as well as that proposed by Singh and co-workers not only show the best fits to the experimental data but also demonstrate that they are the simplest and easiest ones for immediate use.

1 Introduction

The correct design of anaerobic digesters strongly depends on both substrate degradation and biogas production kinetics; thus, the operating conditions of both fed-batch and continuous digestion processes should be selected according to the nature of the starting materials. In this sense, the residues commonly disposed of by this operation, municipal sewage sludges [1,2] and the organic fraction of municipal solid wastes (MSWOF) [3,4] can be regarded as easily-digestible, while lignocellulosics [5] as difficultly-digestible.

There is a certain difficulty in simulating anaerobic digestion through the most common kinetic models for bioprocesses available in the literature not only because of the simultaneous presence of materials with different digestibility in most wastes but also because of the complex interplay existing among hydrolytic, acidogenic, acetogenic, and methanogenic populations [6]. In addition, if in theory a model is simple enough to effectively interpret data, in the practice it often contains as many parameters as possible to be actually and usefully applicable.

Although Cecchi et al. demonstrated that a step diffusional model, taking into account the different stages of hydrolysis, acidogenesis, and methanogenesis, is the best tool to describe the batch digestion of MSWOF [7,8], this model as well as the common biological kinetic models show a significant lack of fit to the experimental data of lignocellulosics degradation, because these residues need nearly complete preliminary hydrolysis of the hemicellulose and lignin fractions [9] and contain about 25–50 % recalcitrant organic matter [10].

In order to study the kinetics of pre-hydrolyzed lignocellulosics fermentation as well as to select the best theoretical approach, batch runs have been carried out at the end of a fed-batch operation under pseudo-stationary conditions. Linearized equations, such as the logarithmic form of the First Order model or the Lineweaver-Burk-type plots of the Monod model, are often used with success to compare the kinetic behaviors of different runs. In fact, although less suited than their original forms to simulate the process progress, they allow a more accurate estimation of the related kinetic parameters. For this reason, the linearized forms of the well-known models of Chen & Hashimoto [11], Monod [12], Inhibition [13], First Order [14], Diffusion [15], Singh [16], and Step-Diffusion [7, 8] have been checked by the fit between the experimental data and the theoretical behaviors of COD degradation described by them.

For practical purposes, it is always preferable to describe the fermentation kinetics using integral methane production (which can easily be followed) instead of COD consumption; this approach, however, requires the knowledge of the ultimate methane yield [11], which is a parameter detectable only with much difficulty at the end of a fermentation of easily-degradable substances. Because of these difficulties, the authors have recently proposed and tested with success a modified version of the First Order model, where the contribution of the recalcitrant fraction to COD consumption kinetics can easily be determined from the COD experimental data [17]. The same approach is extended in this study to the Monod and Chen & Hashimoto models, whose abilities to describe COD degradation versus time for this substrate are compared with those of the other linearized models reported in the literature.

2 Materials and Methods

The experimental set-up, the lignocellulose hydrolyzate preparation, and the measuring methods have recently been described in detail [17]. Batch fermentations were carried out at 37 °C in 3 l glass digesters filled with mesophilic anaerobic sludges from a municipal anaerobic secondary digester.

The feed simulating the composition of agricultural wastes with about 30–40 % difficultly-digestible and recalcitrant

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substances was prepared by mixing 0.678 l of hemicellulose hydrolyzate and 0.299 l of starch hydrolyzate and subsequently diluting the mixture with tap water up to a final volume of 3 l. Variable volumes of this suspension were introduced into the digesters to achieve the desired starting COD. A feed with 50–60 % difficultly-degradable and recalcitrant substances and with a much higher concentration of pentoses was also prepared submitting successive batches of residue from wood acid hydrolysis to a countercurrent washing scheme [18,19].

COD, total dry solids (TDS), and total volatile solids (TVS) concentrations were determined as described in APHA Standard Methods [20]. Biogas production was followed by liquid level displacement. The fractions of methane, carbon dioxide, and nitrogen were determined by gas chromatography.

3 Theoretical Models

The decrease of the substrate concentration occurring during a batch run can be described by several different models proposed in the past for anaerobic digestion. Two adaptations of available models (Monod and First Order models) are proposed in this study to take into account the influence of the relevant fraction of difficultly-digestible substances in the material on the digestion kinetics. The suitabilities of the linearized forms of the models described below have been compared by estimating the determination coefficient (r^2), that is the difference between experimental and theoretical values taken on the whole for each run.

3.1 First Order Model

An overall mass transfer kinetic approach, which thinks of biomass as a catalyst, leads to the First Order kinetic equation [14][1]:

$$-\frac{dC_s}{dt} = k_1 C_s \tag{1}$$

where k_1 is the first order kinetic constant, C_s the concentration of soluble organic substances, and t the fermentation time.

The first order constant has been calculated from the slope of the straight line obtained by plotting $\ln C_s$ versus time. A similar approach has been followed for the other models, transforming all equations into linearized forms suitable for immediate calculation of the kinetic parameters.

3.2 Monod Model

The first attempt to extend the well-known Monod equation to the anaerobic digestion of municipal wastewater treatment

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1) List of symbols at the end of the paper.

sludge was made by Lawrence and McCarty [21]. It was subsequently applied with success to the degradation kinetics of many different wastes whenever methanogenesis could reasonably be assumed as the limiting step [22]:

$$-\frac{dC_s}{dt} = \frac{k_2 C_x C_s}{K_s + C_s} \tag{2}$$

where k_2 is the maximum specific degradation rate, C_x the biomass concentration, and K_s the saturation constant of Monod's equation.

The kinetic parameters k_2 and K_s have been estimated from the slope and intercept of the straight line of the well-known Lineweaver-Burk-type plots and by considering C_x nearly constant. In fact the concentration of microorganisms during fed-batch operation always ranged between 5 and 6 g_{TVS}/l, which is in satisfactory agreement with the values reported by Traverso and Cecchi for the digestion of the shredded MSWOF [23].

3.3 Chen & Hashimoto Model

Chen and Hashimoto [11], adapting the well-known model of Contois [24] to anaerobic fermentation, proposed the following equation to take into account the influence of starting substrate concentration (C_{so}) on the fermentation kinetics of biological systems showing Monod-type growth curves:

$$-\frac{dC_s}{dt} = \frac{k_3 C_x (C_s/C_{so})}{[K + (1 - K) (C_s/C_{so})]} \tag{3}$$

where k_3 is analogous to the maximum specific degradation rate and K is a dimensionless parameter. Also in this case, the concentration of biomass during the fermentations carried out under the selected conditions has been considered constant [7]. This model as well as that of Singh [16] are examples of multi-substrate models that were set up to give a declining reaction rate as the COD is depleted of its most easily-digestible components first.

3.4 Diffusional Model

Previous research clearly demonstrated that substrate-utilization kinetics within biofilms can accurately be described by a model including reaction with diffusion [15,25]. Because digesters not provided with efficient mixing may suffer mass transfer limitation problems by digesting biomass similar to those taking place through biofilms, the diffusion model has also been checked. According to Suidan et al. [15], four different situations may occur within such a reactor:
- the biofilm is deep and the surface substrate concentration very low; in this case the fermentation takes place following pseudo-first order kinetics not depending on the biofilm thickness;

- the biofilm is deep and the surface substrate concentration very high and approaching that in the bulk; the fermentation rate variation with the square root of substrate concentration is typical of a diffusion-limited zero order reaction [15,26]:

$$-\frac{dC_S}{dt} = k_4 \, (C_S)^{0.5} \qquad (4)$$

where k_4 is the related rate constant which can be calculated from the slope of the straight line resulting from integration of this equation;

- the biofilm is fully penetrated and the surface substrate concentration very low; once again, pseudo-first order kinetics would be consistent with the process but the fermentation rate would depend on biofilm thickness;
- the biofilm is fully penetrated and the surface substrate concentration very high and approaching that of the bulk; in this case the fermentation rate should follow zero-order kinetics:

$$-\frac{dC_S}{dt} = k_5 \qquad (5)$$

where k_5 is the related rate constant.

3.5 Singh Model

A modified version of the first order kinetic model was proposed by Singh et al. [16]. During anaerobic digestion, the degradation rate could vary according to the nature of the substrate under consideration, which changes both qualitatively and quantitatively as the digestion process proceeds with time. This necessitates the incorporation of a time function to control the kinetic constant:

$$-\frac{dC_S}{dt} = \frac{k_6 \, C_S}{(1+t)} \qquad (6)$$

where k_6 is the rate constant of the Singh model, which can be calculated from the slope of the straight line obtained plotting $\ln C_S$, after integrating Eq. (6), versus $\ln(1+t)$.

3.6 Modified First Order Model

Since in the presence of a mixture of substrates, the most easily biodegradable substrate is primarily consumed [9,27], a modified version of the First Order model was proposed:

$$-\frac{dC_S}{dt} = k_7 \, (C_S - f \, C_{so}) \qquad (7)$$

which introduced a final COD value, $f \, C_{so}$, at the end of the fermentation of easily-digestible substances.

3.7 Modified Monod Model

For the above reason, the Monod model has also been modified similarly to the equilibrium approach to the enzyme kinetics [28], taking into account the final COD value, $f \, C_{so}$, at the end of fermentation of easily-digestible substances:

$$-\frac{dC_S}{dt} = \frac{k_8 \, C_x \, (C_S - f \, C_{so})}{[K_S' + (C_S - f \, C_{so})]} \qquad (8)$$

where k_8 and K_S' are the corresponding maximum specific degradation rate and saturation constant; the other parameters have been previously defined. The values of k_8 and K_S' have been calculated by the same graphic approach followed for the simple Monod model (Lineweaver-Burk plot) but simultaneously resorting to a trial-and-error procedure for estimating f. The same type of modified equation could be proposed for the Chen & Hashimoto model.

3.8 Step-Diffusional Model

As suggested by Mamie and Lau-Wong [29] and by Cecchi et al. [7,8], anaerobic digestion of complex wastes, containing an easily-digestible, a slowly-degradable, and a recalcitrant fraction, proceeds through three successive stages controlled by methanogenesis, acidogenesis, and biopolymer hydrolysis, respectively.

The consumption of the first fraction, mainly constituted by acetic acid, methanol, and compounds directly convertible into biogas by methanogenic microflora, can be described by the following linearized equation:

$$-\frac{dC_S}{dt} = v_o - k_9 \, t/2 \qquad (9)$$

where v_o and k_9 are the maximum degradation rate for methanogenesis and the related kinetic constant, respectively.

The second fraction, containing volatile fatty acids with more than three C atoms and ethanol, is degraded more slowly according to the equation:

$$-\frac{dC_S}{dt} = v_1 - k_{10} \, (t - t_1)/2 \qquad (10)$$

where $v_1 < v_o$ is the maximum degradation rate related to acidogenesis, k_{10} the related kinetic constant, and t_1 the time required to complete the transformation of the easily-digestible fraction.

Finally, the degradation of the third fraction, mainly constituted of recalcitrant complex biopolymers, is controlled by its hydrolysis and is described by the linearized equation:

$$-\frac{dC_S}{dt} = v_2 - k_{11} \, (t - t_2)/2 \qquad (11)$$

where $v_2 < v_1$ is the maximum degradation rate for hydrolysis, k_{11} the related kinetic constant, and t_2 the time required to complete the transformation of the second fraction.

The above equations, achieved by deriving the degradation rate proportional to the square root of substrate concentration [8], also points out, according to Suidan et al. [15], the diffusional character of this model, which is the result of diffusion limitation due to the presence of insoluble compounds within the digester. Plots of $-dC_s/dt$ versus t allow one to obtain straight lines from whose intercepts and slopes both maximum degradation rates and kinetic constants can easily be estimated.

4 Results and Discussion

A comparison between the above linearized kinetic models and the experimental data was carried out in order to find the model which best describes the behavior of batch anaerobic fermentations of pre-hydrolyzed lignocellulosics. The experimental data of COD consumption during batch fermentations at different starting COD levels are listed in Tab. 1 for both lignocellulose hydrolyzates, containing respectively about 30–40 % and 50–60 % recalcitrant organic substances (slowly metabolizable pentoses, phenols, furfural, hydroxymethylfurfural, incompletely hydrolyzed polymers, etc.).

The COD experimental data have then been used to calculate the kinetic parameters for each of the models presented earlier, at different COD_o values (Tab. 2). A successive comparative analysis of these as well as the estimation of the relative determination coefficient (Tab. 3) allowed us to check their respective ability to describe anaerobic fermentation of this material.

4.1 First Order Model

The application of the First Order model to the COD consumption at different starting COD levels led to the values of the first-order kinetic constant listed in the first line of Tab. 2. Notwithstanding the satisfactory values of r^2, the decrease of k_1 with increasing starting COD raises doubts on the ability of this model, which proved to apply very well to a biofilm reactor [30] and brewery by-products [31], to shed light on the actual phenomenon limiting the anaerobic digestion of this material.

Among the above four different diffusion-limited phenomena consistent with pseudo-first order kinetics, a) a deep biofilm with very low C_s value or b) a fully penetrated biofilm with a very low C_s value were considered to be the most likely for the present case [17]. In both situations, in fact, the decrease of k_1 with increasing COD_o can be ascribed to a growing importance of the recalcitrant fraction in reducing the average diffusivity of the biodegradable substances, as confirmed by the significantly lower value of k_1 obtained

using the hydrolyzate with the higher fraction of recalcitrant substances (COD_o = 7.8 g/l).

4.2 Monod and Chen & Hashimoto Models

Both these models, whose application to the experimental data of COD consumption in this material are shown in Fig. 1, give poor results, as demonstrated by the quite low r^2 values reported in Tab. 3. As previously observed by Cecchi et al. for the anaerobic digestion of the organic fraction of MSW [7], the maximum degradation rate can assume negative values, which does not have actual physical meaning, and these absurd results could not be associated to the linearization technique used for parameter estimation.
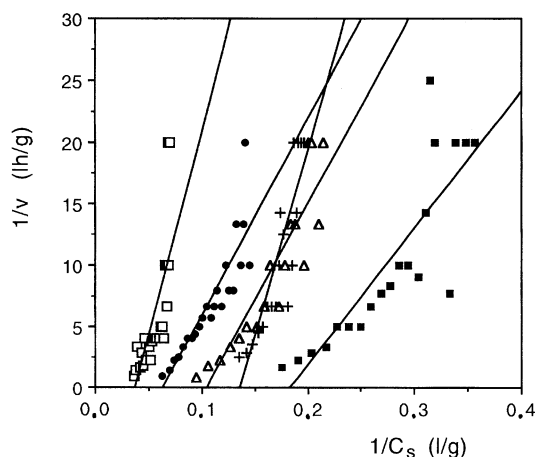

Figure 1. Application of the Monod and Chen & Hashimoto models to the COD consumption during the anaerobic fermentation of pre-hydrolyzed lignocellulosics. Starting COD [g/l]: (■) 6.3; (+) 7.8; (Δ) 13.0; (●) 18.0; (□) 30.0.

As proposed by Roques et al. [32], the saturation constant of the Monod equation may depend, in wastewater treatment as well as in anaerobic digestion, on the sludge age and the biomass concentration in the reactor, thus, causing anomalies in its estimation. Negative values of this constant may also imply equally absurd negative values of the maximum degradation rate. Hence, it can be concluded that both these models are poorly suitable to describe anaerobic digestion of complex materials.

4.3 Diffusional Model

The Diffusion model seems to provide a satisfactory description of the process only at the highest COD_o values. Because of the unsatisfactory fit to the experimental data at low starting COD levels, demonstrated by the lower r^2 values in Tab. 3 with respect to the First Order model and by the curves of Fig. 2, the diffusive phenomenon it describes (deep biofilm with high surface C_s value) is not very likely to be consistent with the actual situation for the process under

Table 1. Experimental COD data during batch fermentation at different starting COD values.

t [h]	COD [g/l]			t [h]	COD [g/l]	
Substrate	A	A	A		B	A
0	30.0	18.0	13.00	0	7.80	6.30
2	27.8	15.8	10.50	1	7.40	5.70
4	26.4	14.4	9.40	2	7.05	5.25
6	25.8	13.5	8.50	3	6.77	4.90
8	25.2	12.7	7.90	4	6.55	4.60
10	24.0	12.1	7.40	5	6.35	4.40
12	23.3	11.6	7.00	6	6.20	4.20
14	22.2	11.1	6.60	7	6.05	4.00
16	21.7	10.6	6.30	8	5.90	3.85
18	20.8	10.2	6.10	9	5.80	3.72
20	20.2	9.90	5.80	10	5.73	3.60
22	19.3	9.60	5.60	11	5.65	3.50
24	18.8	9.25	5.45	12	5.50	3.40
26	18.3	8.95	5.30	13	5.40	3.29
28	17.8	8.71	5.10	14	5.35	3.22
30	17.3	8.40	5.00	15	5.28	3.18
32	16.8	8.21	4.90	16	5.23	3.13
34	16.4	7.96	4.75	17	5.18	3.00
36	16.0	7.70	4.65	18	5.15	2.95
38	15.5	7.55	4.62	19	5.10	2.92
40	15.3	7.35	4.60	20	5.08	2.87
42	15.0	7.19	4.57	21	5.06	2.85
44	14.8	7.10	4.55	22	5.04	2.80
46	14.6	6.90	4.52	23	5.02	2.78

A = Mixture of hydrolyzates with 30–40 % recalcitrant substances; B = Mixture of hydrolyzates with 50–60 % recalcitrant substances

Table 2. Values of the kinetic parameters calculated by the tested models for the anaerobic fermentation of pre-hydrolyzed lignocellulosics.

COD_o [g/l]	6.3	7.8	13.0	18.0	30.0
Substrate	A	B	A	A	A
First Order (Eq. (1)) k_1 [h^{-1}]	0.0314	0.0163	0.0195	0.0186	0.0147
Monod (Eq. (2)) k_2 [g$_{COD}$/g$_{TVS}$ h]	–0.0088	–0.0044	–0.0110	–0.0179	–0.0148
K_s [g$_{COD}$/l]	–5.425	–7.310	–9.513	–15.71	–26.75
Chen & Hashimoto (Eq. (3)) k_3 (g$_{COD}$/g$_{TVS}$ h)	–0.0638	–0.0700	–0.0411	–0.140	–0.136
K [–]	–6.204	–14.91	–2.728	–6.848	–8.227
Diffusional (Eq. (4)) k_4 [g$_{COD}^{0.5}$/l$^{0.5}$ h]	0.0618	0.0397	0.0508	0.0602	0.0657
Singh (Eq. (6)) k_6 [–]	0.2854	0.1559	0.3066	0.2733	0.2229

Table 2 (continued).

COD$_o$ [g/l]	6.3	7.8	13.0	18.0	30.0
Substrate	A	B	A	A	A
Modified First Order (Eq. (7))					
k_7 [h^{-1}]	0.1177	0.1140	0.0787	0.0459	0.0383
f [–]	0.405	0.615	0.331	0.314	0.383
Modified Monod (Eq. (8))					
k_8 [g$_{COD}$/g$_{TVS}$ h]	–0.0231	–0.0279	–0.0403	–0.0586	0.0924
K_s' [g$_{COD}$/l]	–4.421	–4.158	–8.303	–15.993	2.883
f [–]	0.254	0.526	0.231	0.225	0.470
Step-Diffusional (Eqs. (9–11))					
v_o [g$_{COD}$/l h]	0.7167	0.4633	1.550	1.400	1.300
v_1 [g$_{COD}$/l h]	0.2511	0.2298	0.2857	0.3652	0.4905
v_2 [g$_{COD}$/l h]	0.0865	0.0993	0.0875	0.1628	0.1575
k_9 [g$_{COD}$/l h^2]	0.2500	0.1200	0.4000	0.3245	0.2800
k_{10} [g$_{COD}$/l h^2]	0.0354	0.0464	0.0258	0.0304	0.0276
k_{11} [g$_{COD}$/l h^2]	0.0195	0.0128	0.0082	0.0084	0.0350

A = Mixture of hydrolyzates with 30–40 % recalcitrant substances; B = Mixture of hydrolyzates with 50–60 % recalcitrant substances

Table 3. Values of the determination coefficient (r^2) obtained for the tested models by linear interpolation of the experimental data.

COD$_o$ [g/l]	6.3	7.8	13.0	18.0	30.0
Substrate	A	B	A	A	A
First Order	0.923	0.895	0.874	0.957	0.977
Monod and Chen & Hashimoto	0.714	0.771	0.826	0.775	0.464
Diffusional	0.891	0.877	0.823	0.926	0.963
Singh	0.982	0.985	0.982	0.939	0.883
Modified First Order	0.998	0.997	0.995	0.996	0.997
Modified Monod	0.732	0.867	0.860	0.795	0.910
Step-Diffusional					
1st step	0.987	0.991	0.842	0.983	0.891
2nd step	0.891	0.927	0.895	0.891	0.667
3rd step	0.447	0.610	0.747	0.701	0.891

A = Mixture of hydrolyzates with 30–40 % recalcitrant substances; B = Mixture of hydrolyzates with 50–60 % recalcitrant substances

consideration. Therefore, a modification of Eq. (4), necessary to take into account the contribution of the fraction of recalcitrant substances to the digestion kinetics, would not have any physical justification.
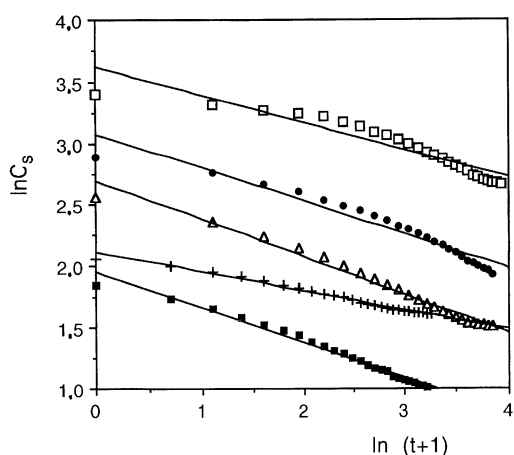
4.4 Singh Model

The model proposed by Singh and co-workers to describe the batch kinetics of cattle waste digestion [16] gives the best results among the linearized traditional kinetic models at low starting COD levels (Tab. 3). The peculiar suitability of this model to difficult waste is due to the incorporation in the first order model of a time function which controls the kinetic constant, thus, accounting for the continuous increase of the recalcitrant fraction with time. Fig. 3 shows the application of this model to both the lignocellulose hydrolyzates tested in this study.

The kinetic parameter k_6 regularly grows with decreasing starting COD (Tab. 2) up to a maximum threshold (COD$_o \approx$ 15 g/l) beyond which it appears to become constant ($k_6 \approx 0.29$). The same influence of recalcitrant substances on the diffusivity of biodegradable compounds, which has been assumed to be responsible for the decrease in k_1 of the First Order model with COD$_o$, can be hypothesized for the Singh
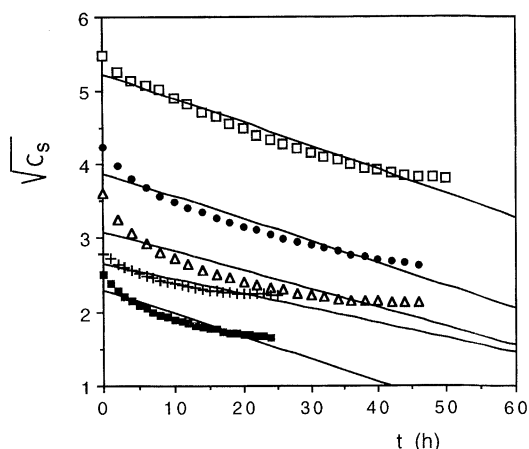
Figure 2. Application of the Diffusion model to the COD consumption during the anaerobic fermentation of pre-hydrolyzed lignocellulosics. Starting COD [g/l]: (■) 6.3; (+) 7.8; (△) 13.0; (●) 18.0; (□) 30.0.

Figure 3. Application of the Singh model to the COD consumption during the anaerobic fermentation of pre-hydrolyzed lignocellulosics. Starting COD [g/l]: (■) 6.3; (+) 7.8; (△) 13.0; (●) 18.0; (□) 30.0.

model, if the diffusion limitation is assumed to be the phenomenon responsible for quasi-first order kinetics. This hypothesis appears to be confirmed by the remarkable decrease of k_6 in the presence of the hydrolyzate with the higher fraction of difficultly-digestible substances ($k_6 = 0.156$). Then, the Singh model demonstrates once more its validity in the description of the anaerobic digestion of complex materials rich in hardly-degradable compounds.

4.5 Modified First Order Model

According to the results in Tab. 3, the Modified First Order model, taking into account the fraction of difficultly-degradable and recalcitrant substances in the feed, best describes the progress of the digestion at all starting COD levels, although the exact nature of the phenomenon (scenarios a or b) most likely responsible for the observed first order kinetics would require further studies at different biomass concentrations.

The f values ensuring the best interpolation for both lignocellulose hydrolyzates ($0.31 < f < 0.40$ for substrate A and $f = 0.61$ for substrate B) are in satisfactory agreement with the fractions of recalcitrant compounds which can be supposed for these wastes (30–40 and 50–60 %, respectively) on the basis of their respective compositions [17].

4.6 Modified Monod Model

As the results in Tabs. 2 and 3 and the curves of Fig. 4 show on the whole, the introduction of f in the Monod equation did not show significant fit enhancement with respect to the simple Monod model, especially as far as the physical meanings of k_8 and K_s' are concerned. In fact, the linear interpolation of the experimental data provides incomprehensible negative values of both the maximum degradation rate and the saturation constant, except for the case with $COD_o = 30$ g/l, even if the calculated values of f are comparable with those calculated by the Modified First Order model.
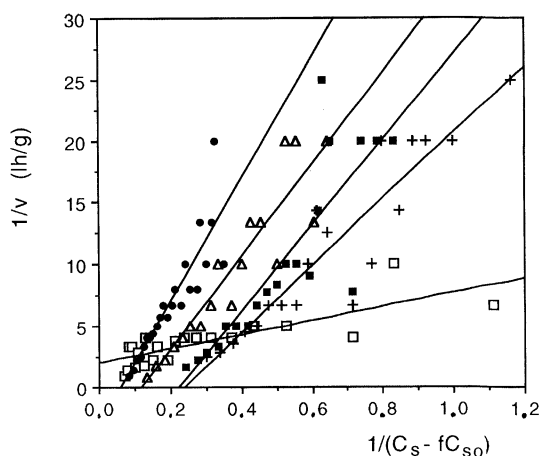
Figure 4. Application of the unfermentable COD fraction to the Monod model. Starting COD [g/l]: (■) 6.3; (+) 7.8; (△) 13.0; (●) 18.0; (□) 30.0.

Not even this attempt to adapt the linearized forms of both the Monod and Chen & Hashimoto models to the kinetic description of difficult organic wastes has provided acceptable results; therefore, it would be reasonable to conclude that they are not suitable for this purpose.

4.7 Step-Diffusional Model

The values of r^2 listed in Tab. 3 demonstrate that the Step-Diffusional model could effectively be applied to describe the anaerobic digestion of pre-hydrolyzed lignocellulosics, when only concerning the easily-digestible and at most slowly-degradable fractions.

The behaviors of COD consumption rate shown in Fig. 5 for $COD_o = 18$ g/l as well as the maximum values of this parameter listed in Tab. 2 for the three different steps demonstrate that the preliminary chemical hydrolysis could be responsible for

the transformation of a relevant fraction of slowly-degradable and recalcitrant materials into easily-digestible ones. In fact, taking the experiment at COD_o = 18 g/l as a reference basis, easily-digestible substances are methanized at a maximum rate (1.40 g_{COD}/l h), which is about four times higher than the maximum acidogenesis rate of the slowly-degradable ones (0.36 g_{COD}/l h). In addition, a comparison with the values reported by other authors for different complex substrates shows that chemical pre-hydrolysis accelerates 5–6-fold the maximum degradation rate for methanogenesis with respect to either mixtures of sewage sludges and separately collected MSWOF or source selected MSWOF [8]. The simple redoubling of the maximum degradation rate for acidogenesis points out that most of the recalcitrant materials contained in the lignocellulosics are transformed by hydrolysis and successive quick acetogenesis into easily-digestible substances rather than into slowly-degradable ones. Nevertheless, preliminary hydrolysis is not enough to completely remove the recalcitrant fraction, which goes on to be very slowly hydrolyzed and removed, after depletion of the second fraction, at a maximum rate that is less than one half (0.16 g_{COD}/l h) the preceding one and only little higher than those which can be estimated for similar complex materials (0.04–0.12 g_{COD}/l h) [8,10].
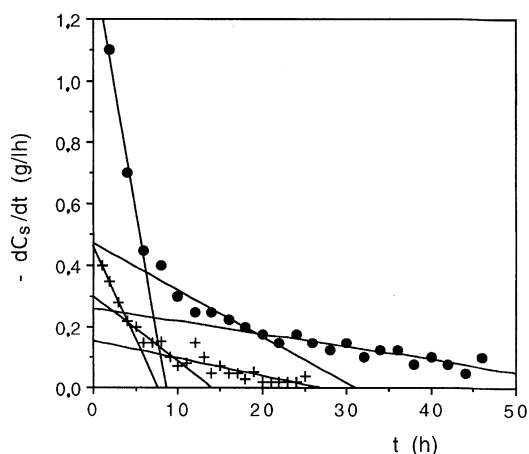
Figure 5. Application of the Step-Diffusional model to the COD consumption during the anaerobic fermentation of pre-hydrolyzed lignocellulosics. Starting COD [g/l]: (+) 7.8; (•) 18.0.

A comparison of the values calculated for the kinetic constants of the three steps (Tab. 2) with those reported by the above authors for other complex materials shows a relevant increase only for methanogenesis (from 0.10-0.18 to 0.32 g_{COD}/l h^2), while the acidogenesis and hydrolysis steps appear to be negligibly influenced.

A marked dependence of maximum degradation rates on starting COD can also be observed when comparing the kinetic parameters listed in Tab. 2. In particular, as far as the maximum degradation rate for methanogenesis (v_o) is concerned, it appears to increase with carbon source availability up to COD_o = 13.0 g/l, according to the diffusional character of this model, while the slow decrease above this

threshold could reasonably be ascribed to the inhibiting effect of excess produced acetate on the metabolism of hydrogenotrophic methanogenic microflora. In other words, an organic and acidic overload takes place in the medium.

Maximum degradation rates of acidogenesis (v_1) and hydrolysis (v_2) show similar behaviors, continuously growing within the COD_o range tested up to a higher threshold (COD_o = 18.0 g/l) before decreasing. This fact suggests that, thanks to their very recalcitrant nature, overload of these substances, although unacceptable because of their tendency to accumulate in the digester, is not so deleterious as that of easily-digestible ones. A similar behavior of the kinetic constant of degradation for methanogenesis can also be observed, whereas no valuable effect can be detected for the other kinetic constants, whose values are at least one order of magnitude less.

Finally, the diffusional character of this model is confirmed once more by the evident decrease in all the kinetic parameters obtained for methanogenesis when feeding the more recalcitrant hydrolyzate (B). This effect can reasonably be ascribed to a marked decrease in easily-digestible substances diffusivities provoked by the presence of a higher fraction of recalcitrant biopolymers in the medium.

5 Conclusions

The present kinetic study of batch fermentations of pre-hydrolyzed lignocellulosic wastes has allowed the identification of which linearized model, among those available in the literature, best represents the behavior of COD degradation during the anaerobic digestion of these materials. Because of preliminary hydrolysis of lignocellulosics, the hydrolysis of biopolymers is no longer the limiting step and the anaerobic digestion may take place at a higher rate.

On the basis of a comparison with the experimental data, some of the most common models proposed for anaerobic digestion, such as those of Monod and Chen & Hashimoto, proved inadequate to represent the actual situation in the digester. Nevertheless, the introduction of a correction factor accounting for the presence of difficultly-degradable and recalcitrant substances in the nutrient has been proposed, with little luck, in this study to enhance their suitability.

On the other hand, among the models modified according to this approach, the First Order model gave results comparable with the Singh model, which already incorporates a time function to control the kinetic constant. Also the Step-Diffusional model provided acceptable, although poorer, results, mainly in simulating the methanogenesis or at most the acidogenesis steps. The phenomenon responsible for the observed kinetics is likely to be the progressive reduction of the average diffusivity of the easily-digestible substances provoked by the parallel increase in the fraction of recalcitrant compounds during the digestion of this material.

Symbols used

COD	[g_{COD}/l]	Chemical oxygen demand
C_s	[g_{COD}/l]	Substrate concentration
C_{so}	[g_{COD}/l]	Starting substrate concentration
C_x	[g_{TVS}/l]	Biomass concentration
f	[–]	Fraction of difficultly-degradable and recalcitrant substances at the end of the fermentation of easily-digestible fraction
k_1	[h^{-1}]	Kinetic constant of the First-Order model
k_2	[g_{COD}/g_{TVS} h]	Maximum specific degradation rate of the Monod model
k_3	[g_{COD}/g_{TVS} h]	Maximum specific degradation rate of the Chen & Hashimoto model
k_4	[$g_{COD}^{0.5}/l^{0.5}$ h]	Kinetic constant of the Diffusional model
k_5	[g_{COD}/l h]	Kinetic constant of the Zero-order model
k_6	[–]	Kinetic constant of the Singh model
k_7	[h^{-1}]	Kinetic constant of the modified First-Order model
k_8	[g_{COD}/g_{TVS} h]	Maximum specific degradation rate of the modified Monod model
k_9	[$g_{COD}/l\ h^2$]	Kinetic constant of the methanogenesis step in the Step-Diffusional model
k_{10}	[$g_{COD}/l\ h^2$]	Kinetic constant of the acidogenesis step in the Step-Diffusional model
k_{11}	[$g_{COD}/l\ h^2$]	Kinetic constant of the hydrolysis step in the Step-Diffusional model
K	[–]	Parameter of Chen & Hashimoto model
K_s	[g_{COD}/l]	Saturation constant of the Monod model
K_s'	[g_{COD}/l]	Saturation constant of the modified Monod model
t	[h]	Time
t_1	[h]	Time required to complete the first step according to the Step-Diffusional model
t_2	[h]	Time required to complete the second step according to the Step-Diffusional model
TDS	[g_{TDS}/l]	Total dry solids
TVS	[g_{TVS} l^{-1}]	Total volatile solids
v_o	[g_{COD}/l h]	Maximum degradation rate for methanogenesis
v_1	[g_{COD}/l h]	Maximum degradation rate for acidogenesis
v_2	[g_{COD}/l h]	Maximum degradation rate for hydrolysis

References

[1] Del Borghi, M.; Solisio, C.; Ferraiolo, G., _La Chimica e l'Industria (Milan)_ 66 (1984) pp. 90–96.
[2] Del Borghi, M.; Solisio, C.; Ferraiolo, G., _La Chimica e l'Industria (Milan)_ 66 (1984) pp. 519–526.
[3] Cecchi, F.; Traverso, P. G.; Clancy, J.; Mata-Alvarez, J.; Zaror, C., _Biomass 16_ (1988) pp. 257–284.
[4] Coombs, J.; Alston, Y. R., _The Potential for Recovery of Energy from Solid Waste Using Fabricated Digester Systems_, in: _Landfill Gas and Anaerobic Digestion of Solid Waste_ (Y.R. Alston, G.E. Richards Eds.), Harwell Laboratory, Oxfordshire, UK, 1989, pp. 454–466.
[5] Ghosh, S.; Henry, M. B.; Christopher, R. W., _Biomass 6_ (1985) pp. 257–269.
[6] Mah, R. A.; Ward, D. M.; Baresi, L.; Glass, T. L., _Ann. Rev. Microbiol. 31_ (1977) pp. 309–341.
[7] Cecchi, F.; Mata-Alvarez, J.; Traverso, P. G.; Medici, F.; Fazzini, G., _Biomass 23_ (1990) pp. 79–102.
[8] Cecchi, F.; Mata-Alvarez, J.; Marcomini, A.; Pavan, P., _Biores. Technol. 36_ (1991) pp. 261–269.
[9] Converti, A.; Drago, F.; Ghiazza, G.; Del Borghi, M.; Macchiavello, A., _J. Chem. Tech. Biotechnol. 69_ (1997) pp. 231–239.
[10] Mata-Alvarez, J.; Cecchi, F., _Kinetic Models Applied to the Anaerobic Biodegradation of Complex Organic Matter_, in: _Biotechnology and Biodegradation_ (D. Kamely, A. Chakrabardy, G.S. Omenn Eds.), Portfolio Publ. Co., The Woodland, TX, 1989, pp. 317–344.
[11] Chen, Y.; Hashimoto, A., _Biotechnol. Bioeng. Symp. 8_ (1978) pp. 269–282.
[12] Monod, J., _Annu. Rev. Microbiol. 3_ (1949) pp. 371–376.
[13] Ierusalimsky, N. D., _Microbial Physiology and Continuous Culture_ (E.O. Powell, C.G.T. Evans, R.E. Strange, D.W. Tempest Eds.), Her Majesty's Stationary Office, London, 1967, pp. 23–33.
[14] Pfeffer, J. T., _Biotechnol. Bioeng. 16_ (1974) pp. 771–787.
[15] Suidan, M. T.; Ritmann, B. E.; Traegner, U. K., _Wat. Res. 21_ (1987) pp. 491–498.
[16] Singh, R.; Jain, M. K.; Tauro, P., _Wat. Res. 17_ (1983) pp. 349–351.
[17] Converti, A.; Rezzani, L.; Del Borghi, M., _J. Air & Waste Manag. Assoc. 48_ (1998) pp. 174–178.
[18] Strickland, R. C.; Beck, M. J., Effective Pretreatments and Neutralization Methods for Ethanol Production from Acid-catalyzed Hardwood Hydrolyzates Using _Pachysolen tannophilus_. Paper presented at 6th Int. Symp. on Alcohol Fuels Technol., Ottawa, 21–25 May 1984.
[19] Perego, P.; Converti, A.; Zilli, M.; Del Borghi, M., _Bioproc. Eng. 10_ (1994) pp. 35–41.
[20] APHA, _Standard Methods for the Examination of Water and Wastewater_, 14th Edition, APHA, AWWA, WPCF, Washington, DC, 1975.
[21] Lawrence, A. W.; McCarty, P. L., _J. Wat. Pollut. Control Fed. 41_ (1969) pp. R1–R17.
[22] Chin, K. K., _Wat. Res. 15_ (1981) pp. 199–202.
[23] Traverso, P. G.; Cecchi, F., _Biomass 6_ (1988) pp. 97–106.
[24] Contois, D.E., _J. Gen. Microbiol. 21_ (1959) pp. 40–50.
[25] Rittmann, B. E.; McCarty, P. L., _J. Envir. Eng. Div. Am. Soc. Civ. Engrs 107_ (1981) p. 831.
[26] Harremoes, P., _Biofilm Kinetics_, in: _Water Pollution Microbiology_ (R. Mitchell Ed.), Wiley, New York, 1978.
[27] Di Berardino, S.; Bersi, R.; Converti, A.; Rovatti, M., _Bioproc. Eng. 16_ (1997) pp. 65–70.
[28] Roels, J. A., _Energetics and Kinetics in Biotechnology_, Elsevier Biomedical, Amsterdam, 1983, p. 166.
[29] Lau-Wong, M. M., _The Effect of Operational Parameters on Biogas Production and a Comparison of the Dynamics of Three Reactor Designs_, in: _Proc. 4th Int. Symp. on Anaerobic Digestion_, Guangzhou, China, 1985, pp. 191–207.
[30] Canovas-Diaz, M.; Howell, J. A., _Biotechnol. Bioeng. 32_ (1997) pp. 348–355.
[31] Keenan, J. D.; Kormi, I., _Biotechnol. Bioeng. 19_ (1977) pp. 867–878.
[32] Roques, H.; Yue, S.; Saipanich, S.; Capdevill, B., _Wat. Res. 16_ (1982) pp. 839–847.