Full Length Article

Kinetic modelling of anaerobic co-digestion of sewage sludge and Sherry-wine distillery wastewater: Effect of substrate composition in batch bioreactor

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ABSTRACT

Batch thermophilic anaerobic co-digestion of sewage sludge (SS) and Sherry-wine distillery wastewater (SW-DW) was investigated through biochemical methane potential tests (BMP). The results pointed out that biodegradability and biomethane potential were enhanced proportionally to the percentage of SW-DW of the feedstock, whose soluble biodegradability fraction is 10-fold higher than SS. Specifically, organic matter removal increases from 37 % (employing sole SS as feedstock) to 60 % (employing sole SW-DW as feedstock). SW-DW almost doubles methane yield in comparison to SS (302 ± 15 and 175 ± 9 NL/kg, respectively).

A structured kinetic model was developed considering hydrolysis, acidogenic and methanogenic steps of anaerobic digestion. A non-linear multiple-response regression was employed to estimate the kinetic parameters for each feedstock (0%(v/v) SW-DW, 25%(v/v) SW-DW, 50%(v/v) SW-DW, 75%(v/v) SW-DW, and 100%(v/v) SW-DW). The first-order kinetic parameter estimated of the hydrolysis step varies inversely proportional to the percentage of SW-DW content in the feedstock. Whereas, there is no significant influence of feedstock composition on kinetic parameters value regarding acidogenesis and methanogenesis. These results showed that rate–limiting step switched during the fermentation and the addition of SW–DW favours acidogenic and methanogenic steps. In summary, the proposed kinetic model was able to predict batch experimental data, supporting the application of biogas production from anaerobic co-digestion of SS and DW-DW.

1. Introduction

Wine production is part of the economic engine in the Mediterranean societies. Specifically, Sherry-wine is the most important wine produced in Cadiz region (South of Spain) having an under cultivation area higher than 7100 ha and more than 36 million of litres produced in 2020 [1]. However, associated to the industrial production process, Sherry-wine distillery wastewater (SW-DW) is generated as a by-product composed by a mixture of liquid waste from pressing and first fermentation phases of wine processing, the bottom of the distillery unit, grape juice spillage and chemical cleaning products from equipment and tanks. SW-DW is considered one of the most important environmental concerns in viticulture agro-industries due to its strongly acid pH, the high organic load and its cytotoxic components, such as polyphenolic derivatives [2]. In addition, the seasonality of the wine production also implies an issue for the waste management at full-scale [3].

The application of biological aerobic and anaerobic treatments is a promising technology to reduce the organic matter content in SW-DW [2,4–6]. Comparing to the aerobic processes, the anaerobic digestion (AD) treatment presents great advantages, such as low operating costs, a well-known understanding of the available technology, and biogas production during the treatment, which could eventually cover part of the energy requirements in the plant. Recently, the use of SW-DW as co-substrate in AD of municipal sewage sludge (SS) has been already started studying [3,7–9]. And yet, the addition of co-substrates derived from meat industry, such as chicken manure and poultry manure, are emerging researches [10,11]. Anaerobic co-digestion (ACoD) presents many advantages, including shared treatment facilities, reducing initial investment and operating costs, buffering of the variations in the composition of the waste over time and dilution of toxic compounds [12].

It is well-known that, AD takes places by means of a complex reaction

network involving several steps and a large number of microbial species. Overall, AD is lumped in four serial steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. However, there are many other steps that occur in series and parallel reactions, such as butyrate-degrading acetogenesis, acetoclastic, hydrogenotrophic methanogenesis, propionate degradation, and inhibition by pH and high concentration of acid components [13]. The overall rate of AD will be controlled by the slowest stage of the process, known as the rate-limiting step. Although, some authors describe that the hydrolysis of wastes with a high content of solid organic matter controls the AD due to the mass transfer limitations, it is also accepted that acetogenesis or methanogenesis might be the rate-controlling step in AD of complex wastes [14,15].

Kinetic model of anaerobic treatment systems plays a key role to develop and controlling more stable processes [16]. It is also a powerful tool in the scale-up of bioprocesses. To date, a large number of published papers aim to describe biogas production of AD, considering only the last step of the process. Through simple kinetic equations, such as first-order, logistic, Cone, and Gompertz model, cumulative methane production is successfully fitted and predicted for batch experiments [17–21]. However, this mathematical approach limits to describe biogas evolution over time without considering the connection between the generation of the final product and the organic matter consumption. In order to provide a more comprehensive AD model, a further kinetic description focusing on the involving metabolic pathways is required. In this sense, only few researchers have developed complex kinetic modelling of AD considering the relationship between enzymatic hydrolysis, acidogenesis, acetogenesis and methane production. Most of them included first-order kinetic and Monod-type equations to describe the degradation of different wastes, such as livestock manure [22,23], olive pomace [13], orange rind [24], organic fraction of municipal solid waste [25], microalgae [14], cow manure [26] and SS [27].

The present work aimed to develop a kinetic model to describe the anaerobic co-digestion of SS and SW-DW at thermophilic temperature (55 °C) in batch bioreactor. In order to reach this goal, the influence of feedstock composition on biodegradability and biomethane production was studied in biochemical methane potential (BMP) tests. Based on the experimental tendencies over the time, a kinetic model including hydrolysis, acidogenic, and methanogenic steps was proposed. Finally, a comparison of the estimated kinetic parameters was conducted to study the influence of feedstock composition on the rate-limiting step. This is the first time that kinetic modelling of ACoD of SS and SW-DW was developed.

2. Material and methods

2.1. Inoculum and substrates

The wastes used as substrates in the present study came directly from industrial features located in Jerez de la Frontera (Cadiz, Spain). SS were collected from a secondary treatment floatation unit from Guadalete wastewater treatment plant. SW-DW was obtained from Gonzalez-Byass, an ethanol producing wine-distillery plant. Both substrates were kept under refrigeration at 4 °C until use to avoid biodegradation.

Different mixtures of SS and SW-DW, as well as sole SS and sole SW-DW, were used as substrates to evaluate the biomethane potential of each waste. Five mixtures were tested as substrate in BMP test, being its proportion of SW-DW 0, 25, 50, 75, and 100 % (v/v). The pH values of co-digestion mixtures were in a range of 6.0–7.0. Before it used, pH was adjusted to 7.8–8.2 using sodium hydroxide solution (2 M). The characteristics of each raw substrate and inoculum are summarised in Table 1.

The effluent of 5 L laboratory-scale mesophilic anaerobic digester was used as inoculum in the BMP test. The reactor was operated under semi-continuous mode setting with a hydraulic retention time of 20 d and feeding with activated SS. According to the established considerations in literature to standardize protocol for BMP assays [28,29],

Table 1
Inoculum and raw substrates characteristics.

Parameter	Inoculum	SS	SW-DW
pH	7.8 ± 0.2	6.9 ± 0.2	6.4 ± 0.2
CODt (kg/m^3)	19.9 ± 0.4	53.9 ± 1.2	24.6 ± 2.2
CODs (kg/m^3)	9.7 ± 0.3	19.0 ± 0.3	20.7 ± 0.6
TS (kg/m^3)	2.09 ± 0.03	3.67 ± 0.01	1.47 ± 0.11
vS (kg/m^3)	1.21 ± 0.01	2.69 ± 0.03	1.06 ± 0.09
Alkalinity (kg/m^3)	5.81	3.53	0.02
VFA (kg/m^3)	0.41	2.85	0.75
TN (kg/m^3)	2.15	14.8	1.09
C/N	9.2	5.2	17.5

inoculum was stored at 55 °C for 7 days before employing in batch tests in order to deplete the residual biodegradable organic material present in it. This step is highly recommended to minimize endogenous methane production of the inoculum and assuring the reproducibility of the assays.

2.2. Biomethane potential tests

BMP tests were carried out in order to evaluate biodegradability and biogas production that can be potentially reached by ACoD treatment of each substrate.

Batch reactors employed in BMP tests were 250 mL serum bottles with a working volume of 130 mL. The initial broth composition was 60 % (v/v) of substrate, and 40 % (v/v) of inoculum. All bottles were subsequently purged with 100 % N_2 for 3–4 min in order to achieve anaerobic atmosphere for the run. BMP tests took place in an orbital shaker at 85 rpm under thermophilic conditions (55 ± 1 °C). Control run, containing only anaerobic inoculum and distillate water, was performed to determine background gas production. For each mixture, eight runs were conducted initially. Every 3–4 days, a duplicate was used to analyse medium composition in terms of total and soluble chemical oxygen demand (CODt, and CODs), total and volatile solids (TS, and VS), and volatile fatty acids (VFA) content.

BMP tests were performed until daily methane production meant less than 1 % of total (25 days). Biomethane production data relating to produced volume and biogas composition showed in this paper correspond to the average daily values of each bottle.

2.3. Analytical methods

pH, TS, vS CODt, and CODs were determined according to Standard Methods [30]. pH determination was taken by pHmeter type CRISON MICROPH 2001 with a temperature probe. For TS, vS and FTS, samples were weighed in ceramic boats in a laboratory balance Cobos type and drying in oven type ELF14 de CARBOLITE.

VFA (acetic, propionic, isobutyric, butyric, isovaleric, valeric, isocaproic, caproic and heptanoic acid) were determined by gas chromatography (GC-2010 Plus Shimadzu). Total acidity was calculated by summing up the individual fatty acids in terms of equivalent mass of acetic acid.

Gas composition was determined employing a gas chromatography technique (GC-2010 Shimadzu). The analysed gases (H_2, CH_4, CO_2, O_2 and N_2) were measured by means of a thermal conductivity detector (TCD) at 250 °C using a Supelco Carboxen 1010 Plot column. The oven temperature was programmed between 35 and 200 °C. Manual injection was carried out employing a sample volume of 250 mL. The carrier gas was helium at 35 kPa of pressure.

2.4. Mathematical methods

Aspen Custom Modeler v10 software (AspenTech, USA) was employed to fit the kinetic model to experimental data in order to estimate kinetic parameters. The set of differential equations forming the

kinetic model were integrated using the numerical implicit Euler method. A multiple-response method to fit the model to the data was set. The kinetic parameters were estimated by minimizing the difference between experimental observations and model simulations according to "least squares method" by an adaptive non-linear least-squares algorithm (NL2SOL).

For the porpoise of the validation regarding the proposed model, physicochemical and statistical criteria were performed, including:

- F-Fischer's value (F), which should be higher than its tabulated value at 95 % confidence (F_{95}) to fulfil the null hypothesis.
- Sum of squared residuals (SSR), which should be as close to zero as possible.
- Residual mean square error (RMSE), which should be as close to zero as possible.
- Percentage of explained variance (VE), which should be equal or near 100 % to indicate an identical change of experimental and simulated data with time.

3. Results and discussion

3.1. Substrate biodegradability and methane production in BMP tests

Substrate biodegradability was evaluated based on initial and final characteristics in BPM test. Physicochemical characteristics measured at the beginning and at the end in serum bottles for each experiment are shown in Table 2.

In general, organic matter is reduced in terms of CODt, TS and vS though the batch AD process for all the employed substrates. The removal percentage of each parameter has been calculated in order to discuss the influence of the substrate composition. As it is shown in the Fig. 1, the presence of SW-DW in the substrate has a positive effect on the biodegradability of the feedstock: the higher SW-DW content, the higher CODt (Fig. 1A), TS (Fig. 1C) and vS removal (Fig. 1D). While in contrast, only around 37 % of CODt and vS are reduced when SS is employed as carbon source, 50 % of the organic matter is degraded in the mixture 50 % SS – 50 % SW-DW and values up to 60 % are reached employing raw SW-DW. These results showed that SW-DW contains more soluble and easily metabolized organic matter, which promotes ACoD in comparison to sole SS AD. Similar improvement of SS biodegradability by adding SW–DW as co-substrate in AD has been previously reported in mesophilic temperature range [7].

Moreover, operational temperature has a perceptible effect on CODs removal. Whereas mesophilic temperature range an effective CODs

Table 2
Initial and final characteristics of substrates in serum bottles.

| Parameters (kg/m³)	SW-DW (%)				
	0	25	50	75	100
CODt_initial	50.1 ± 0.3	46.8 ± 0.4	38.4 ± 0.9	36.0 ± 1.4	31.5 ± 1.6
CODt_final	31.0 ± 0.5	25.0 ± 1.1	19.5 ± 1.5	17.8 ± 1.1	12.4 ± 0.1
CODs_initial	11.0 ± 1.7	11.9 ± 1.1	15.4 ± 0.6	17.8 ± 0.8	21.6 ± 0.5
CODs_final	14.8 ± 1.0	14.0 ± 0.6	10.0 ± 0.2	10.5 ± 0.8	8.7 ± 0.9
TS_initial	36.9 ± 0.1	35.0 ± 0.1	31.7 ± 0.1	28.3 ± 0.2	24.7 ± 0.7
TS_final	28.5 ± 0.2	25.4 ± 0.3	22.2 ± 0.2	19.3 ± 0.2	15.1 ± 0.3
VS_initial	26.1 ± 0.3	24.5 ± 0.2	21.7 ± 0.4	19.3 ± 0.2	15.7 ± 0.1
VS_final	16.9 ± 0.4	14.2 ± 0.4	11.3 ± 0.4	8.7 ± 0.2	4.7 ± 0.6
VFA_initial	1.1 ± 0.1	1.5 ± 0.1	0.8 ± 0.1	1.4 ± 0.1	1.1 ± 0.1
VFA_final	2.7 ± 0.1	2.5 ± 0.1	2.8 ± 0.1	2.5 ± 0.1	2.0 ± 0.1
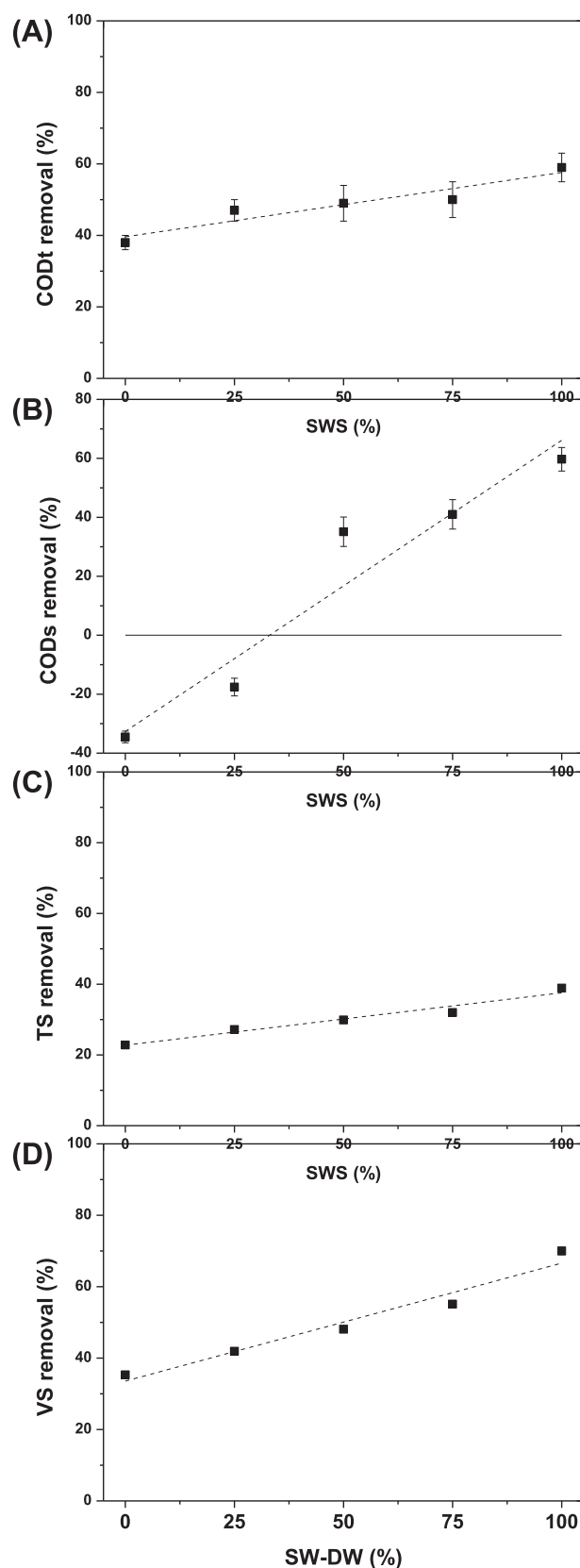
Fig. 1. Influence of waste composition on CODt removal, CODs removal, TS removal, and vS removal in BMP test.

removal was showed independently the proportion of SW-DW added [7], in thermophilic temperature range lower SW-DW proportion than 30 % in the feedstock leads to an accumulation of soluble organic matter in the final effluent, as it is showed in Fig. 1B on the negative values of CODs removal. For higher values of SW-DW than 30 %, an effective consumption of soluble organic matter is achieved, reaching CODs degradation between 40 and 60 %. However, in all those cases VFA were accumulated in the effluent respect to the initial VFA content (Table 2). As it will be seen in the biomethane production results, VFA production did not inhibit biogas generation.

Regarding the methane production, Fig. 2 shows the influence of feedstock composition on methane yield, which was calculated as the quotient of the cumulative volume of produced methane at the end of the experiment over the initial organic matter content in terms of volatile solids. It is noteworthy that the methane yield increases when the amount of SW-DW increases in co-digestion even though, the initial vS content is lower than vS presenting in SS. In spite of the above-mentioned differences relating to solubilisation of organic matter, the obtained results of methane production in thermophilic temperature range are quite similar to the previously published in batch runs at mesophilic temperature range [7]. In short, these results support the organic matter containing in the waste derived from distillery industry is highly biodegradable and its addition as co-substrate in SS digestion improves methane production.

3.2. Kinetic modelling of anaerobic co-digestion

The kinetic modelling of AcoD has been based on the evolution of particulate chemical oxygen demand (CODp) (defined as the difference between CODt and CODs), CODs, acetic acid (AA), and methane (CH_4). Based on the experimental results, a structured kinetic model was proposed to describe the macroscopic observed tendencies related to CODp, CODs, AA, and methane production. In order to develop a kinetic model to describe AD experiments, the following considerations were taken into consideration:

- Batch bottles were considered as completely mixed bioreactors.
- At first, particulate substrate (CODp) must have been hydrolysed to obtain an accessible soluble substrate (CODs).
- The high-molecular-weight compounds containing in the accessible soluble substrate were transformed into acetic acid, the final and simplest volatile fatty acid in acetogenesis step.
- Finally, AA is transformed into methane by means of aceticlastic methanogenesis pathway.
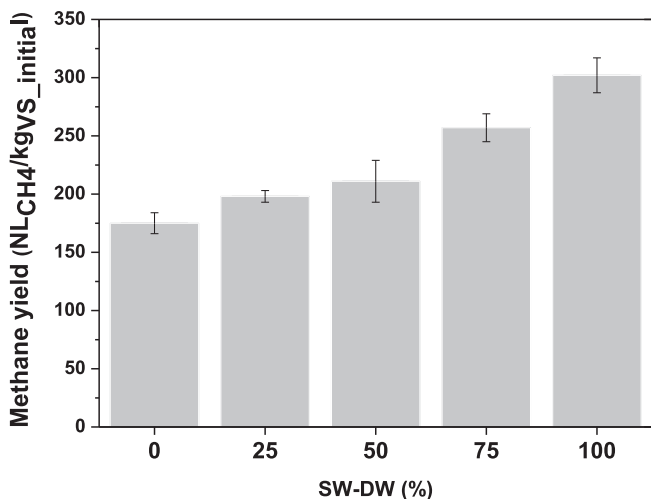

Fig. 2. Influence of feedstock composition on methane yield reached at the end of BMP tests.

- Since hydrogen production was negligible during the experiments, hydrogenotrophic methanogenesis pathway was not considered in the kinetic description of the process.
- All concentrations, except methane production, were expressed as COD. Therefore, it is necessary to define the yield methane from COD ($Y_{CH4/COD}$), a pseudo-stoichiometric coefficient in macroscopic terms.
- Employed substrates, SS and SW-DW, were partially biodegradable, as it had been previously suggested for other organic wastes [24]. Therefore, the fraction of non-biodegradable particulate substrate (CODp_nb) and the fraction of non-biodegradable soluble substrate (CODs_nb) have been considered in the kinetic model.
- A first-kinetic order kinetic equation was proposed for each step.
- Deviations in conservation of mass derived from water evaporation and biomass adhesion to the bioreactor's surface was assume as negligible, as other authors also previously assumed [13,24]

Taking this information into consideration, the following kinetic model was developed. The simplified reaction network is composed by 3 steps: hydrolysis, acetogenesis and methanogenesis, as is showed in Eq. (1)–(3). For each step, a first-kinetic order reaction rate was defined, as is showed in Eq. (4)–(6). Based on this information, a differential equation regarding the production rate of each component involved was established, as is showed in Eq. (7)–(10).

Hydrolysis step.

$$CODp \xrightarrow{r_1} CODs \tag{1}$$

Acetogenic step.

$$CODs \xrightarrow{r_2} AceticAcid \tag{2}$$

Methanogenic step.

$$AceticAcid \xrightarrow{r_3} Y_{CH4/AA}·CH_4 \tag{3}$$

$$r_1 \left(kg_{COD}/m^3·d\right) = k_1·[[CODp] - CODp\_nb] \tag{4}$$

$$r_2 \left(kg_{COD}/m^3·d\right) = k_2·[[CODs] - CODs\_nb] \tag{5}$$

$$r_3 \left(kg_{COD}/m^3·d\right) = k_3·[AA] \tag{6}$$

$$\frac{d[CODp]}{dt} \left(kg_{COD}/m^3·d\right) = -k_1·[[CODp] - CODp\_nb] \tag{7}$$

$$\frac{d[CODs]}{dt} \left(kg_{COD}/m^3·d\right) = k_1·[[CODp] - CODp\_nb] - k_2·[[CODs] - CODs\_nb] \tag{8}$$

$$\frac{d[AA]}{dt} \left(kg_{COD}/m^3·d\right) = k_2·[[CODs] - CODs\_nb] - k_3·[AA] \tag{9}$$

$$\frac{d[CH_4]}{dt} \left(NL_{CH4}/m^3·d\right) = Y_{CH4/AA}·k_3·[AA] \tag{10}$$

The fitting of the proposed kinetic equation to experimental data (CODp, CODs, AA and methane) for each BMP run was carried out to estimate the value of the kinetic parameter involving the kinetic model. Fig. 3 shows the fit of the values predicted by the model to the experimental data over the time for each mixture SS:SW-DW evaluated as substrate.

In general, particulate substrate content decreases over the time as a consequence of the hydrolysis of solid molecules such as carbohydrates, proteins and lipids is taking place. The higher particulate organic matter content linked to the higher SS proportion leads to a faster consumption at the beginning of the fermentation. The evolution of soluble organic matter is the net result of two opposing steps: hydrolysis and acetogenesis, which causes the production and the consumption of CODs,
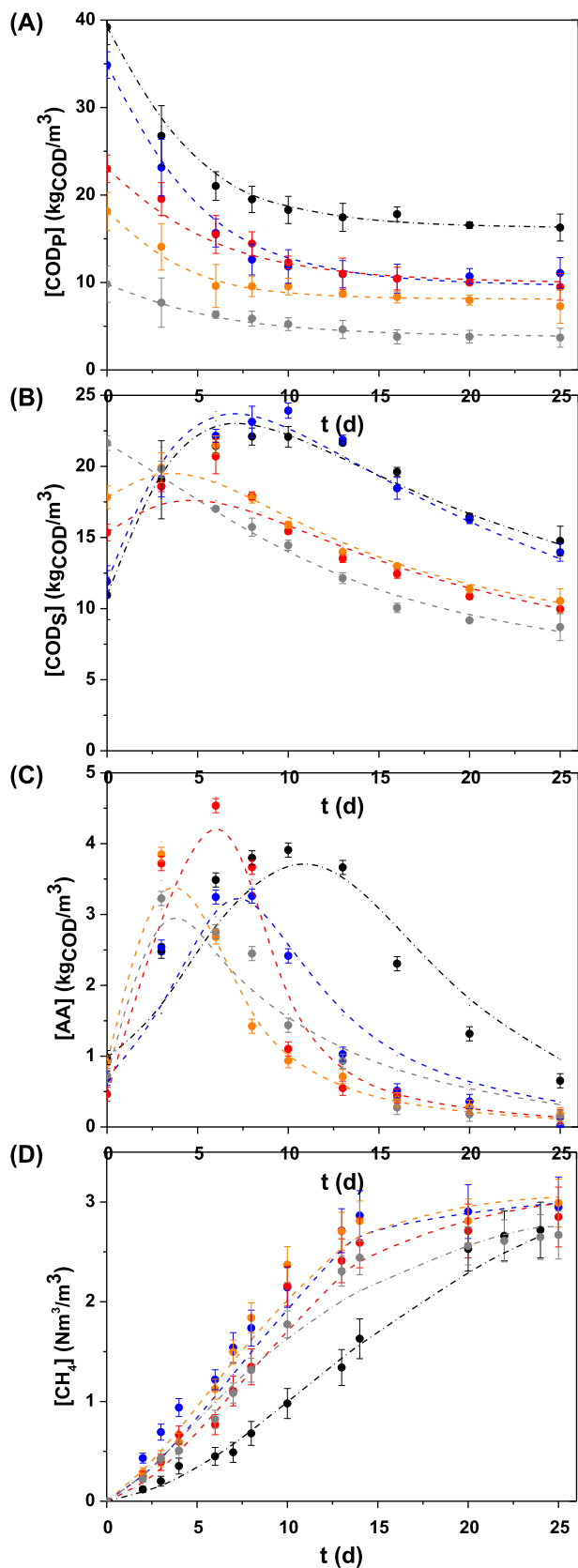
respectively. Consequently, a peak in CODs content is observed. However, SW-DW content in the feedstock increases the initial accessible soluble substrate that leads to slighter maximum tendencies. Even more, evolution of soluble organic matter is always decreasing over the time when sole SW-DW is used as sole carbon source (Fig. 3B), which means that acetogenesis rate takes place faster than hydrolysis during the whole experiment. The evolution of acetic acid also follows the typically tendency of an intermediate compound, increasing at the beginning of the fermentation due to the acidogenic step and decreasing afterwards due to its consumption in methanogenic step. However, the maximum value is achieved at shorter periods of time with the increasing of SW-DW in the feedstock. AA concentration reached the maximum at 10 h when sole SS was employed, whereas the peak is observed around 7 h ahead (at 3 h) when sole SW-DW was used (Fig. 3C). Regarding methane production, its concentration increases over the time as final product in the reaction network. Accordingly to AA exhaustion, methane production reaches a plateau at the end of the batch fermentation. It should be pointed out that the faster methane production is observed in co-digestion runs (25 %, 50 % and 75 % SW-WD) due to the combination of high total and soluble organic matter presenting in theses feedstock.

Table 3 shows the estimated kinetic parameters, as well as the statistical parameters that provide the information on the goodness of fit. The proposed model fits reasonably to all relevant data. Goodness-of-fit statistical parameters indicate a high value for Fisheŕs F, very much over the limiting value (the value of the F tabulated at 95 % was 8.6), and a low value for the RMSE and the SSR. Moreover, the experimental tendencies and the predicted from the model are quite similar, as the VE percentages higher than 90 % showed.

The influence of feedstock composition on the value of the kinetic parameters is shown in Fig. 4. The fractions of non-biodegradable particulate and soluble substrates follow a linear tendency with the composition of the employed feedstock. Assuming that non-biodegradable content was presented initially in the wastes, SS has 41.4 % of non-biodegradable particulate organic matter and 93.6 % of non-biodegradable soluble organic matter. In the case of SW-DW, the non-biodegradable fraction is around a third: only 38.4 % of the particulate matter and 31.0 % of the soluble matter are non-metabolizable. Regarding the first-order kinetic parameter of hydrolysis step, k_1 also depends directly on the composition of the employed substrate, being proportional to the ratio of the mixture. More specifically, the faster hydrolysis takes places when SS is used as substrate probably due to its higher content in solid particles. On the other hand, first-order kinetic parameter of acidogenic and methanogenic steps, k_2 and k_3, are around the same value independently the feedstock composition. A similar tendency is observed for the pseudo-stoichiometric coefficient $Y_{CH4/COD}$. Based on these results, feedstock composition affects basically hydrolysis kinetics in anaerobic co-digestion of SS and SW-WD, which address the resulting differences in waste degradation and biogas production.

In order to determine the rate-limiting step, the evolution of the reaction rate of each step in BMP tests was calculated for each mixture SS:SW-DW employing estimated kinetic parameters values and predicted concentration profiles, as it is shown in Fig. 5. In general, reaction rate of hydrolysis step (r_1) decreases over the time due to the ongoing consumption of particulate organic matter. In all the cases, r_1 eventually tends to zero, which is relating to the total exhaustion of the biodegradable particulate content of the wastes. The higher initial particulate content leads to a faster initial rate and a longer required time to be entirely consumed. Except for 100 % of SW-WD, the reaction rate of acidogenesis step (r_2) reaches a peak around the crossing point of hydrolysis with acidogenesis rates, which regards to the maximum amount of soluble COD in the system. In AD of sole SW-WD (Fig. 5E), r_2 is maximal at the beginning of the experiment just as the soluble organic matter content (Fig. 3B). The reaction rate of methanogenic step (r_3) follows a similar tendency than acidogenesis rate, showing similar values in the second part of the experiments (since around 5 h of fermentation). Methanogenic step is completely limited by acetic acid

Fig. 3. Experimental evolution (points) and kinetic model prediction (dashed lines) of (A) particulate, (B) soluble organic matter, (C) acetic acid concentration, and (D) methane production in the BMP tests. **Key**: (SW-DW percentage in feedstock composition) black: 0%; blue: 25%; red: 50%; orange: 75%; grey: 100%. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3

Kinetic and statistical parameter values calculated by fitting the kinetic model to experimental data of BMP experiments for each substrate.

0 % SW-DW

Kinetic parameters		Statistical parameters	
COD_{p_nb} (kg_{COD}/m^3)	16.2 ± 0.4	F / F_{95}	2390
COD_{s_nb} (kg_{COD}/m^3)	10.3 ± 1.5	RMSE	0.55
k_1 (d^{-1})	0.23 ± 0.01	SSR	11.3
k_2 (d^{-1})	0.09 ± 0.01	VE (%)	98.0
k_3 (d^{-1})	0.29 ± 0.03	–	–
$Y_{CH4/COD}$ (NL_{CH4}/kg_{COD})	156 ± 19	–	–

25 % SW-DW

Kinetic parameters		Statistical parameters	
COD_{p_nb} (kg_{COD}/m^3)	11.6 ± 0.6	F / F_{95}	1020
COD_{s_nb} (kg_{COD}/m^3)	9.1 ± 0.9	RMSE	0.79
k_1 (d^{-1})	0.21 ± 0.01	SSR	23.9
k_2 (d^{-1})	0.08 ± 0.01	VE (%)	96.6
k_3 (d^{-1})	0.57 ± 0.06	–	–
$Y_{CH4/COD}$ (NL_{CH4}/kg_{COD})	186 ± 17	–	–

50 % SW-DW

Kinetic parameters		Statistical parameters	
COD_{p_nb} (kg_{COD}/m^3)	9.9 ± 0.8	F / F_{95}	1686
COD_{s_nb} (kg_{COD}/m^3)	8.6 ± 1.2	RMSE	0.75
k_1 (d^{-1})	0.18 ± 0.02	SSR	21.5
k_2 (d^{-1})	0.11 ± 0.02	VE (%)	93.3
k_3 (d^{-1})	0.44 ± 0.05	–	–
$Y_{CH4/COD}$ (NL_{CH4}/kg_{COD})	202 ± 24	–	–

75 % SW-DW

Kinetic parameters		Statistical parameters	
COD_{p_nb} (kg_{COD}/m^3)	8.1 ± 0.4	F / F_{95}	1120
COD_{s_nb} (kg_{COD}/m^3)	7.8 ± 0.9	RMSE	0.54
k_1 (d^{-1})	0.17 ± 0.02	SSR	11.4
k_2 (d^{-1})	0.11 ± 0.02	VE (%)	95.2
k_3 (d^{-1})	0.54 ± 0.05	–	–
$Y_{CH4/COD}$ (NL_{CH4}/kg_{COD})	203 ± 14	–	–

100 % SW-DW

Kinetic parameters		Statistical parameters	
COD_{p_nb} (kg_{COD}/m^3)	3.8 ± 0.3	F / F_{95}	2840
COD_{s_nb} (kg_{COD}/m^3)	6.7 ± 0.6	RMSE	0.29
k_1 (d^{-1})	0.15 ± 0.02	SSR	3.5
k_2 (d^{-1})	0.12 ± 0.01	VE (%)	98.5
k_3 (d^{-1})	0.51 ± 0.04	–	–
$Y_{CH4/COD}$ (NL_{CH4}/kg_{COD})	183 ± 9	–	–

formation, which can also be seen in the comparable trend of AA with COD_s showed in Fig. 3C. The lower values of AA concentration in comparison to COD_s ones favours that r_3 is limited by the previous step in the reaction network, r_2.

The slowest rate performs as the rate-limiting step and it controls the overall rate. In BMP tests the rate-limiting step changes along the fermentation, being methanogenic reaction at shorter periods of time and hydrolysis reaction at longer periods of times. For 100 % of SW–WD, hydrolysis step is always de controlling phenomena due to its higher initial soluble organic matter. In conclusion, the addition of SW-WD as co-substrate in SS reduces the role of solubilisation of organic matter step in AD and, as a result, biomethane production is favoured as it was shown in Fig. 2. This fact must be taking into account for the optimization of the hydraulic retention time of the process under continuous operational mode.
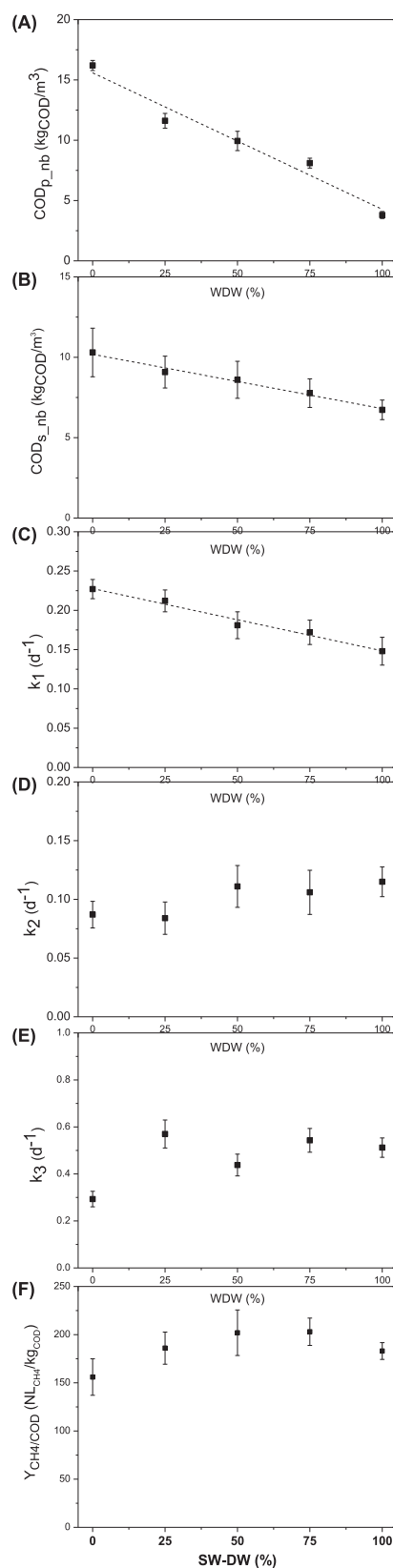
Fig. 4. Influence of on SW-DW percentage in feedstock composition on the kinetic parameter value: (A) fraction of non-biodegradable particulate substrate (COD_{p_nb}), (B) fraction of non-biodegradable soluble substrate (COD_{s_nb}), (C) first-order kinetic parameter of hydrolysis step (k_1), (D) first-order kinetic parameter of acidogenic step (k_2), (E) first-order kinetic parameter of methanogenic step (k_3), and (F) pseudo-stoichiometric coefficient yield methane from COD ($Y_{CH4/COD}$).
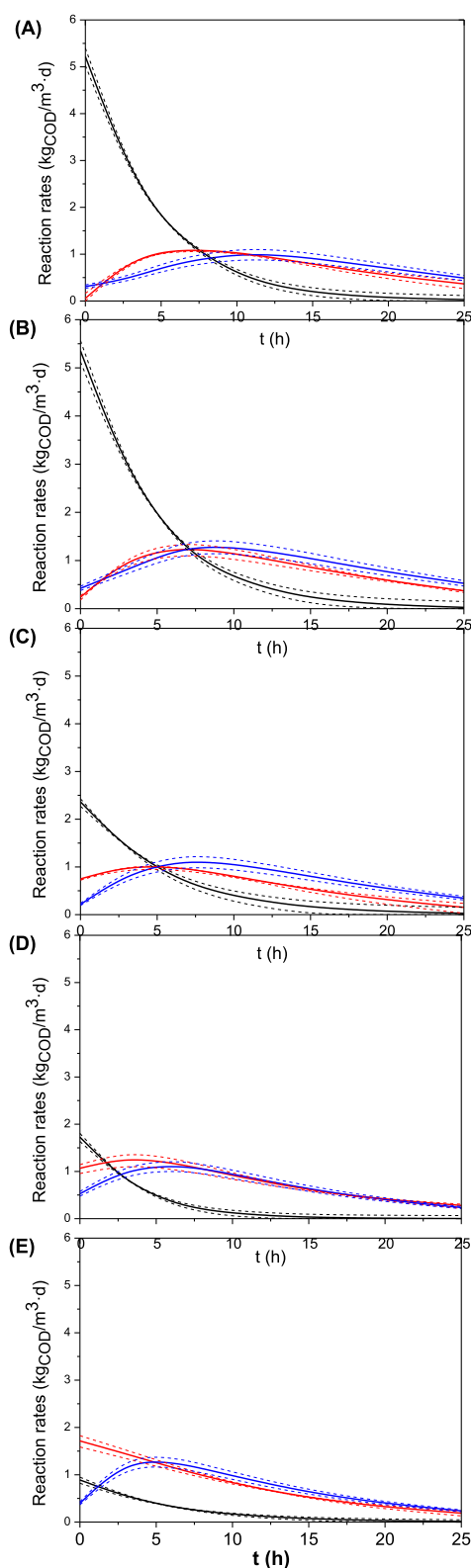
Fig. 5. Evolution of predicted reaction rate of each step (hydrolysis, acidogenesis and methanogenesis) in BMP test employing different SW–DW proportion in feedstock: (A) 0%, (B) 25%, (C) 50%, (D) 75%, and (E) 100%. *Key:* black: hydrolysis step, red: acidogenic step, blue: methanogenic step. Solid lines: model prediction. Dashed-lines: model prediction considering error range of estimated parameters. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Conclusions

Revalorization of agro-industrial wastes through anaerobic co-digestion contributes to develop the concept of biorefinery in the framework of circular economy proposed by H2020 EU program. In this sense, kinetic modelling is a powerful tool to provide useful information on the overall performance of the process for the scaling up.

The addition of SW-DW, as a co-substrate in anaerobic digestion of SS, enhances feedstocks biodegradability as well as biomethane production. These improvements are linked to the higher particulate and soluble biodegradable fractions of SW-DW (61.6 % and 69.0 %, respectively) in comparison to SS (58.6 % and 6.4 %, respectively).

A kinetic model considering hydrolysis, acidogenic, and methanogenic steps was developed that successfully reproduces experimental data supporting by statistical criteria (F–Fischer's value, sum of squared residuals, residual mean square error, and percentage of explained variance). The percentage of SW-DW of feedstock has an inverse effect on hydrolysis kinetic parameter and, therefore, on hydrolysis step rate. Regarding acidogenesis and methanogenesis, substrate composition does not influence the value of kinetic parameters involving in each step.

Analysing the rate-limiting step along the fermentation, methanogenic step limits the overall rate at shorter periods of time whereas hydrolysis step do it at longer times. In addition, SW-DW plays an important role whithin switching the mechanism of methane production, where acidogenesis and methanogenesis steps are enhanced since the beginning due its higher initial soluble organic matter. This consideration might be decisive to design and control the process in continuous operational mode.

CRediT authorship contribution statement

Vanessa Ripoll: Conceptualization, Methodology, Validation, Formal analysis, Writing – original draft. **Rosario Solera:** Conceptualization, Resources, Writing – review & editing, Project administration, Funding acquisition. **Montserrat Perez:** Conceptualization, Resources, Writing – review & editing, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

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