Environmental Pollution 287 (2021) 117605

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

S/X ratio impacts the profile and kinetics of carboxylic acids production from the acidogenic fermentation of dairy wastewater☆

Amanda de Sousa e Silva, Tasso Jorge Tavares Ferreira, Naassom Wagner Sales Morais, Erlon Lopes Pereira, André Bezerra dos Santos *

Department of Hydraulic and Environmental Engineering, Federal University of Ceará, Fortaleza, Ceará, Brazil

ARTICLE INFO

Keywords:
Acidogenic fermentation
Dairy wastewater
Carboxylic acids
S/X ratio
Kinetic modeling

ABSTRACT

The acidogenic fermentation of dairy wastewater (DW) was evaluated for carboxylic acids (CA) production, investigating the influence of substrate/microorganism (S/X) ratio and applying different mathematical models to the bioproduct formation data. The experiments were performed in batch reactors for 28 days, and four S/X ratios were tested (0.8, 1.2, 1.6, and 1.9 gCOD $gVSS^{-1}$). The S/X ratio increase did not influence the percentage of DW conversion into carboxylic acids (42–44%), but the productivity was positively affected (100–200% in general). Acetic acid was the CA formed in the highest concentration for all experiments, followed by propionic and butyric acids. Exponential models were better suited to describe this kinetics process. Therefore, according to the estimated kinetic parameters, the S/X ratio 1.6 was more suitable for CA production from acidogenic fermentation of dairy wastewater, in which the concentrations of longer CA, such as propionate and butyrate, were formed in higher quantities. In addition, it was determined a correlation between the S/X ratio and kinetic parameters like degradation/production rate constant (K) and maximum productivity rate (μ_m).

1. Introduction

The interest in reducing the dependence on the petrochemical platform for fuel and chemicals production is receiving significant attention, which accounts for about 90% of the market demand for carboxylic acids (CA). They are chemical blocks of high added value and several industrial applications such as the production of varnishes, paints, perfumes, disinfectants, surfactants, textile auxiliaries, medicines, and food products (Du et al., 2015; Murali et al., 2017).

However, due to environmental impacts, risk of scarcity, and high oil prices, CA production from biorefineries is an alternative to producing fuels and chemicals from raw materials such as starch and sugar (edible crops - first generation) (Abdulkhani et al., 2017), wastewater, residual glycerol, and wheat straw (non-edible and biodegradable biomass - second generation) (Atasoy et al., 2018), and algae (third-generation) (Du et al., 2015; Moncada B et al., 2016; Romero-García et al., 2018; Sawatdeenarunat et al., 2016). Among these raw materials, the second generation stands out as an opportunity to add value to wastes, often employing anaerobic digestion (AD) processes (Lovato et al., 2015; Silva et al., 2020).

In the AD process, complex organic matter is transformed into monomers (hydrolysis) that are converted into short-chain carboxylic acids (primary and secondary fermentation) which are used as substrates for the formation of methane (methanogenesis) or combined with compounds rich in energy to form more complex compounds like medium- or long-chain CAs (Cavalcante et al., 2017; Kucek et al., 2016). A positive point for using agro-industrial wastewaters (AWWs) as substrates for CA production is that there are already many anaerobic treatment plants in operation worldwide that can be converted into biorefineries for CA production (Silva et al., 2020; Strazzera et al., 2018). Among these AWWs, dairy wastewater (DW) is a promising substrate for CA production because of its high content of energy and organic matter (McAteer et al., 2020). According to data from the Food and Agriculture Organization of the United Nations ((FAO 2019)), world milk production in 2018 was estimated at 843 million tonnes. The production of wastewater can vary from 0.2 to 10 L per liter of processed milk, with a biochemical oxygen demand (BOD) range from 40 to 48, 000 mg L^{-1} and chemical oxygen demand (COD) from 80 to 95,000 mg L^{-1}, which represent a potential risk, especially for the aquatic environment, if there is no proper destination (Ahmad et al., 2019; Buntner

☆ This paper has been recommended for acceptance by Jörg Rinklebe.

* Corresponding author. Department of Hydraulic and Environmental Engineering, Campus do Pici, Bloco 713, Pici, CEP: 60455-900, Fortaleza, Ceará, Brazil.
E-mail address: andre23@ufc.br (A. Bezerra dos Santos).

https://doi.org/10.1016/j.envpol.2021.117605
Received 1 June 2020; Received in revised form 20 April 2021; Accepted 17 May 2021
Available online 16 June 2021

et al., 2013; Markou et al., 2017; Silva et al., 2020). Therefore, the organic load of this type of wastewater is very high, making the CA recovery economically feasible (Ahmad et al., 2019; Buntner et al., 2013; Silva et al., 2020).

However, several parameters can influence this process, such as substrate composition, inoculum concentration, organic load, substrate/microorganism (S/X) ratio, hydraulic retention time (HRT), solids retention time (SRT), pH, temperature, among others (Coma et al., 2017). Understanding the influence of the S/X ratio is emphasized since studies on this parameter are scarce in the literature, and high S/X ratio values may lead to a higher capacity of CA production. Silva et al. (2020) explored the anaerobic resource conversion from some AWWs employing the CA biorefinery platform and showed conversion yields from 67 to 1,176 mg CA g $COD^{-1}_{applied}$. For this platform to be economically viable, it is necessary to achieve the highest possible yields, i.e. the maximization of CA production in acidogenic fermentation. Additionally, it is worth achieving high added-value products, which are sometimes formed in low/moderate concentrations and may depend on the S/X ratio used (Liu et al., 2017).

Mathematical modeling methods are an alternative that can be used to control and predict the performance of anaerobic treatment systems, making it possible to estimate important kinetic parameters to design and operate biological treatment plants more efficiently, which generates significant economic payback (Abou-Elela et al., 2016; Ebrahimi et al., 2018). Kaewsuk et al. (2010) evaluated the kinetic of methanogenic anaerobic digestion of DW, and recently Coelho et al. (2020) studied the kinetic of acidogenic fermentation of DW. More information about models for anaerobic digestion can be found in the reviews of Kythreotou et al. (2014) and Maleki et al. (2018). Additionally, the S/X ratio may influence the oxidative and reductive pathways involved in the anaerobic production of carboxylic acids. However, none of the works cited previously evaluated the impacts of this parameter on the profile of carboxylic acids formed and on the process kinetics.

In this context, we assessed the effect of the substrate/microorganism (S/X) ratio in the production of CA from the acidogenic fermentation of real dairy wastewater using a microbiome that had chemical inhibition of methanogenesis. Different mathematical models to acidogenic fermentation data were applied to select those that best describe the process and estimate the kinetic parameters correlated with the S/X operational parameter.

2. Materials and methods

2.1. Substrate and inoculum

The dairy wastewater (DW) was collected from a dairy industry located in Maranguape, Ceará, Brazil. The inoculum used was sludge from an Upflow Anaerobic Sludge Blanket (UASB) reactor that treated domestic sewage. Total solids (TS), total volatile solids (TVS), and total fixed solids (TFS) of the inoculum were 72.7, 44.8, and 27.9 g L^{-1}, respectively.

2.2. Experimental design

The experiments were carried out in three batch reactors, using borosilicate flasks with 300 mL total volume (270 mL reaction volume and 30 mL of headspace). The experiment evaluated four substrate/microorganism ratios (S/X) where the inoculum concentration was fixed (2.5 gVSS L^{-1}), and the substrate concentrations were varied by diluting the raw DW to obtain 0.8, 1.2, 1.6, and 1.9 gCOD $gVSS^{-1}$. These experiments were carried out at the same experimental period, in a parallel way.

The basal medium and pH 7.0 buffering, previously adjusted with 1 M HCl or NaOH, were performed according to Dams et al. (2018). Also, chloroform 0.05% (v/v) was added to inhibit methanogenesis (Viana et al., 2019). The reactors were sealed with rubber stoppers and purged with nitrogen gas (N_2) for 1 min to guarantee an anaerobic environment. Subsequently, the flasks were kept in an Incubator (Shaker), model Marconi MA-420, under circular agitation at 150 rpm and 35 °C for 28 days (Coelho et al., 2020). Liquid samples were collected on days 0, 2, 4, 7, 14, 21, and 28 to analyze the chemical oxygen demand (COD) and quantification of the formed bioproducts (alcohols and carboxylic acids). At the end of the experiment (28th day), a 1 mL sample of biogas was collected from the headspace of each reactor to determine the average levels of CH_4, H_2, CO_2, and H_2S.

2.3. Analytical methods

The pH, COD, and solids analyses were performed according to the Standard Methods for the Examination of Water and Wastewater (APHA, 2017). The biogas composition was analyzed by a gas chromatograph with discharge detection by dielectric barrier ionization (GC BID-2010 Plus, Shimadzu Corporation, Japan). The method used was the one described by Morais et al. (2019).

Carboxylic acids (CA) were quantified by high-performance liquid chromatography (HPLC) (model 20-AT, Shimadzu Corporation, Japan), with UV/VIS detector and Supelcogel 8H cross-linked column (30 cm × 7.8 mm DI, 9 μm). The oven temperature was 60 °C, 5 mM H_2SO_4 mobile phase, flow ranging from 0.6 to 1.2 mL min^{-1}, and running time of 40 min. The chromatography samples were filtered on a glass fiber membrane with 0.45 μm porosity (EMD Millipore, USA) and centrifuged at 13000 rpm for 6 min (Eppendorf AG, Germany) to avoid interference in the analyses.

The alcohol 1,3-propanediol (1,3-PD) was analyzed in a gas chromatography-flame ionization detection (GC-FID) (Trace GC Ultra, Thermo Scientific, USA), equipped with a capillary column FFAP-CP (25 m × 0.32 mm, ID 0.3 μm) from Agilent Technologies (Netherlands). The samples were diluted with ultrapure water (Milli-Q system, EMD Millipore, USA) in a 1:1 ratio to a final volume of 2 mL directly in borosilicate glass vials (20 mL) for extraction of the headspace (10 min at 120 °C) (Supelco, USA), which were sealed with PTFE/silicone septa and aluminum seals (Supelco, USA), according to Monteiro et al. (2016) with modifications. The detector, injector, and oven temperatures were 250, 200, and 40 °C, respectively. Hydrogen was the carrier gas, and the flow conditions were 1.5 mL min^{-1} for 9 min.

2.4. Mass balance, yields, and kinetic study

Calculations of mass balance, yield, selectivity, and productivity of bioproducts were performed according to Morais et al. (2019), with slight conceptual modifications. The soluble COD that was not in the form of carboxylic acids was considered as the sum of recalcitrant, liable to be bio converted or unidentified carboxylic acids fractions. The equations used are found in Table S1. Kinetics of the soluble substrate consumption, which can be converted into bioproducts, was described using the following mathematical models: First-order, First-order with Residual, Logistics, and Monod with growth; for the generation of bioproducts were the First-order, First-order with Residual, Logistics, Monod with growth, Second-order, Fitzhugh, Cone, BPK, Monomolecular, Modified Gompertz, Logistics, Transfer, and Richards model (Table S2).

The calculation of kinetic parameters and the adherence of mathematical models to the kinetic process was performed according to Yang et al. (2016). The data obtained experimentally were analyzed statistically using Microcal Origin 8.1 software (Microcal Software Inc., Northampton, MA, USA), through analysis of variance (ANOVA) with a 95% confidence level and 5% probability ($p < 0.05$). Tukey's tests were used to compare the different treatments (S/X ratios of 0.8, 1.2, 1.6, and 1.9). Thus, the data were presented using the average value followed by the statistical treatment letter, where equal letters mean no significant difference for $p < 0.05$. The determination coefficient R^2 and Akaike information criterion (AIC) were used to select the model that best

Table 1
Final mass balance of the acidogenic fermentation process from dairy wastewater in different S/X ratios.

S/X	Final Mass Balance		
	$COD_{SNB}/COD_{T\ apl}$	$COD_{CA}/COD_{T\ apl}$	$COD_{VSS}/COD_{T\ apl}$
0.8	0.51 ± 0.03^{a}	0.42 ± 0.01^{b}	0.06 ± 0.00^{c}
1.2	0.54 ± 0.01^{a}	0.42 ± 0.02^{b}	0.04 ± 0.00^{c}
1.6	0.52 ± 0.03^{a}	0.44 ± 0.04^{b}	0.04 ± 0.00^{c}
1.9	0.52 ± 0.02^{a}	0.44 ± 0.03^{b}	0.04 ± 0.00^{c}

Notes: $COD_{T\ apl}$: total COD applied to the reactor at the beginning of the experiment (residual glycerol + organic matter from seed sludge); COD_{CA}: COD converted carboxylic acids identified in the chromatographic method used (HLa, HAc, HPr, HBu, HIVa, and HVa); COD_{SNB}: Soluble COD except identified carboxylic acids (recalcitrant, liable to bioconversion, and unidentified bioproducts); COD_{VSS}: COD for cell growth. The same letters mean that there was no significant difference ($p < 0.05$).

describes organic matter conversion, as described in Coelho et al. (2020).

3. Results and discussion

3.1. Effect of the S/X ratio on the distribution of bioproducts profile and productivity

Initially, part of the particulate organic matter was hydrolyzed, and together with the initial soluble COD, was transformed mainly into carboxylic acids (CA). The conversion of the applied organic matter into CA and cell growth was about 52–54% and 4–6%, respectively, for all S/X ratios studied (Table 1). The 1,3-PD was not found in any S/X ratio tested. Besides, methane was not found in the biogas, which proves the effective inhibition of methanogens by chloroform, promoting CA accumulation (Dams et al., 2018). The S/X ratio increase did not affect CA percentage conversion likely because there was a proportional increase of complex biodegradable organic matter, such as lipids and proteins, that could not be converted into CA by the microorganisms present in the inoculum (Elangovan and Sekar, 2012).

However, it is important to highlight that bioproducts' profile varies over time and with the different S/X ratios tested, as shown in Fig. 1. At the beginning of the experiments (day 0), HLa and HAc were only quantified in the highest S/X ratios tested (1.6 and 1.9), where there was a higher quantity of DW, representing approximately 1% of the total COD applied. In general, over the experiments, there was a production of acetic, propionic, and butyric acids, and a discreet iso-valeric formation in the last two weeks. At the end of all the experiments, the CA formed in the highest quantity was acetic acid, a similar result obtained by Silva et al. (2019) during the anaerobic digestion of dairy wastewater under mesophilic conditions in a fluidized-bed reactor operated with organic loading rates (OLR) of 28.65, 53.2 and 95.8 kgCOD m^{-3} d^{-1}.

However, the COD percentage of HAc decreased with the increment in the S/X ratio. No significant reduction in the percentage of HPr and HBu was found for S/X ratios of 1.6 and 1.9. Therefore, the fraction of

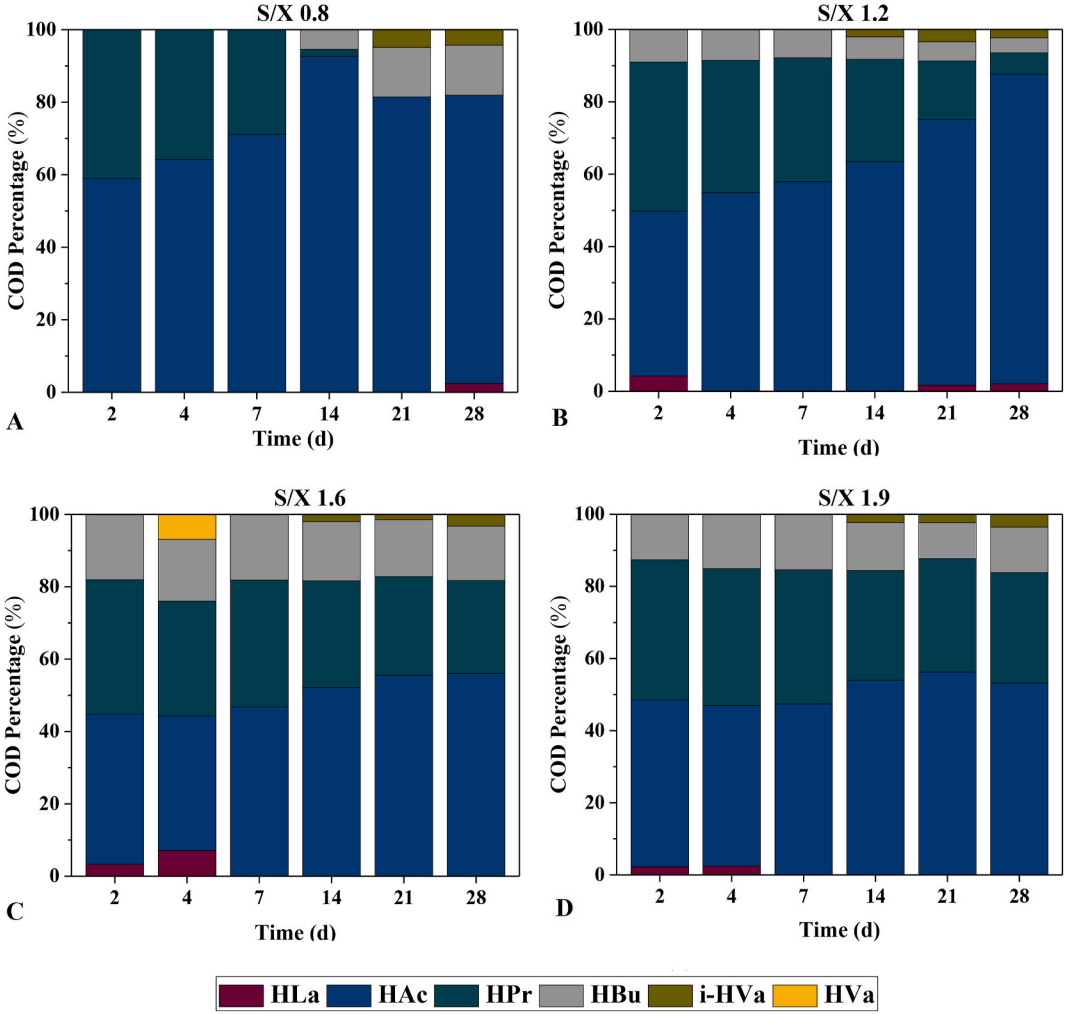

Fig. 1. Carboxylic acids profile over time in the process of acidogenic fermentation of dairy wastewater for the S/X ratios of 0.8 (A), 1.2 (B), 1.6 (C), and 1.9 (D).

Table 2
Concentration and yield of the carboxylic acids identified at the end of the experiments of acidogenic fermentation from dairy wastewater in different S/X ratios.

Carboxylic Acid	Concentration (mg L^{-1})				Yield - Y_{BP} (mg $gCOD_{T\ apl}^{-1}$)			
	S/X Ratio							
	0.8	1.2	1.6	1.9	0.8	1.2	1.6	1.9
HLa	18 ± 0^{a}	21 ± 0^{b}	–	–	9 ± 0^{a}	7 ± 0^{b}	–	–
HAc	732 ± 2^{a}	1077 ± 65^{b}	1109 ± 132^{b}	1355 ± 77^{c}	361 ± 1^{a}	372 ± 22^{a}	279 ± 33^{b}	278 ± 16^{b}
HPr	–	52 ± 11^{a}	358 ± 130^{b}	548 ± 18^{c}	–	18 ± 4^{a}	90 ± 33^{b}	113 ± 4^{b}
HBu	75 ± 27^{a}	31 ± 10^{b}	174 ± 62^{c}	188 ± 67^{c}	37 ± 14^{a}	11 ± 3^{b}	44 ± 16^{a}	39 ± 14^{a}
i-HVa	21 ± 14^{a}	15 ± 1^{b}	33 ± 5^{c}	48 ± 3^{d}	10 ± 7^{a}	5 ± 0^{b}	8 ± 1^{a}	10 ± 1^{a}
HVa	–	–	–	–	–	–	–	–
CA_T	847 ± 44^{a}	1197 ± 87^{b}	1676 ± 330^{c}	2141 ± 167^{d}	418 ± 22^{a}	414 ± 31^{a}	422 ± 84^{a}	442 ± 36^{a}

Notes: : not detected; HLa: lactic acid; HAc: acetic acid; HPr: propionic acid; HBu: butyric acid; i-HVa: iso-valeric acid; HVa; valeric acid; CA_T: total carboxylic acid. The same letters mean that there was no significant difference ($p < 0.05$).

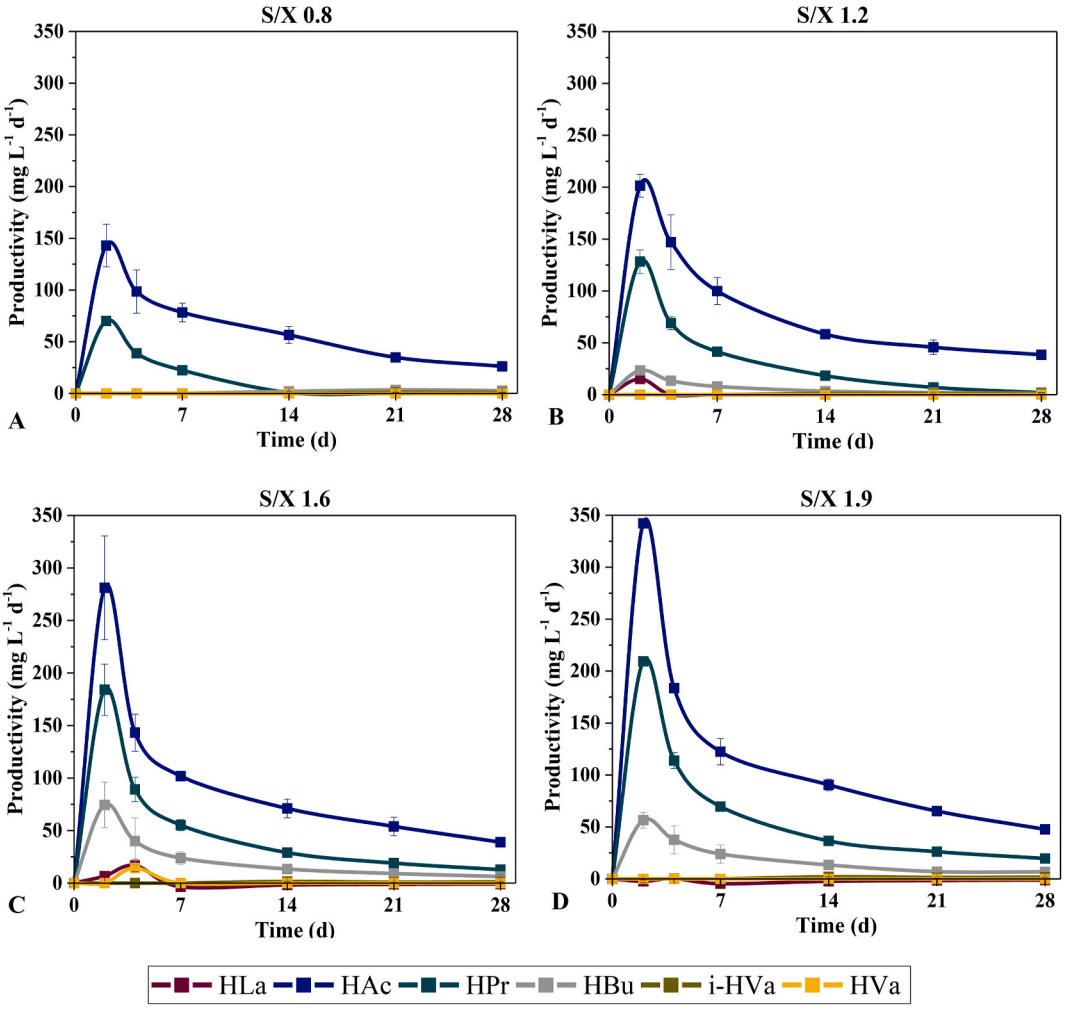

Fig. 2. Bioproducts productivity over time in the process of acidogenic fermentation of dairy wastewater for the S/X ratios of 0.8 (A), 1.2 (B), 1.6 (C), and 1.9 (D).

HAc was lower, probably due to a higher partial pressure of hydrogen that prevents oxidation of HPr and HBu (Bastidas-Oyanedel et al., 2015). Therefore, the design and operation of anaerobic processes using high S/X ratios were more attractive in resource recovery from DW fermentation, as these higher chain carboxylic acids have a higher commercial interest. This conclusion can be better understood when analyzing the concentration and yield of these CAs (Table 2). The yield (Y_{CA}) of HPr in the S/X ratio 1.6 was five times higher than in the S/X ratio 1.2, and when increasing the S/X to 1.9, there was an increase of 25%; the concentration of HPr also enhanced with the increase in S/X. For HBu, there was no significant difference in Y_{CA} between S/X 0.8, 1.2, and 1.6. However, there was an increase in the concentration from 75 to 174 and 188 mg L^{-1}, respectively, facilitating a subsequent extraction of this acid (Xiong et al., 2015).

Furthermore, the increase of the S/X ratio caused an increase in CA productivity (Fig. 2). In general, the maximum productivity was achieved on the second day of the experiment: 342 mg L^{-1} d^{-1} for HAc (at S/X ratio 1.9), 209 mg L^{-1} d^{-1} for HPr (at S/X ratio 1.9), and 74 mg L^{-1} d^{-1} for HBu (at S/X ratio 1.6). Comparing with the productivity obtained at S/X ratio 0.8, also on the second day, there were increases of 139% and 199% for HAc and HPr, respectively. From the third day onwards, there was an exponential decrease in productivity, with

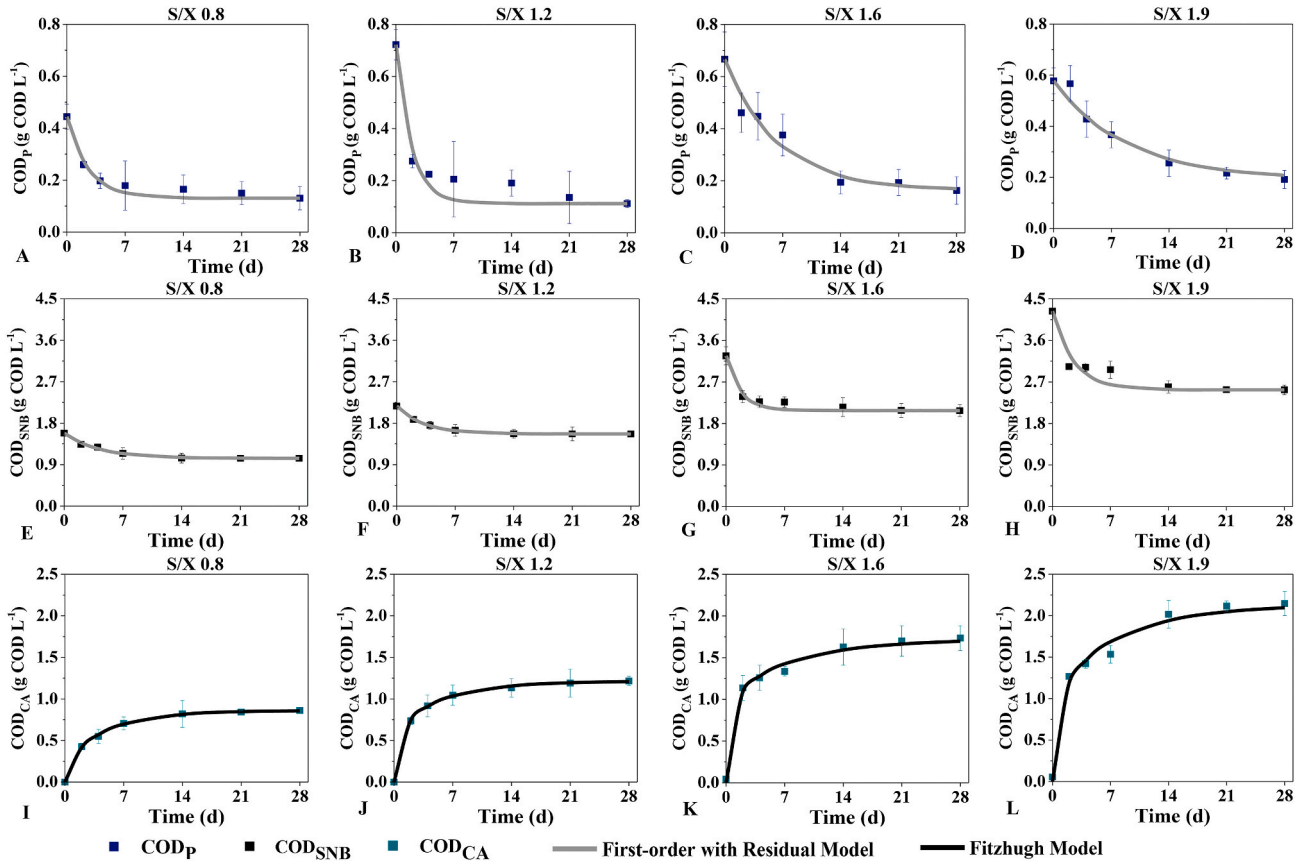

Fig. 3. Kinetic curves of hydrolysis (First-order with Residual model), substrate consumption (First-order with Residual model), and kinetic modeling of carboxylic acids production in the form of COD (Fitzhugh model) for the different S/X ratios tested.

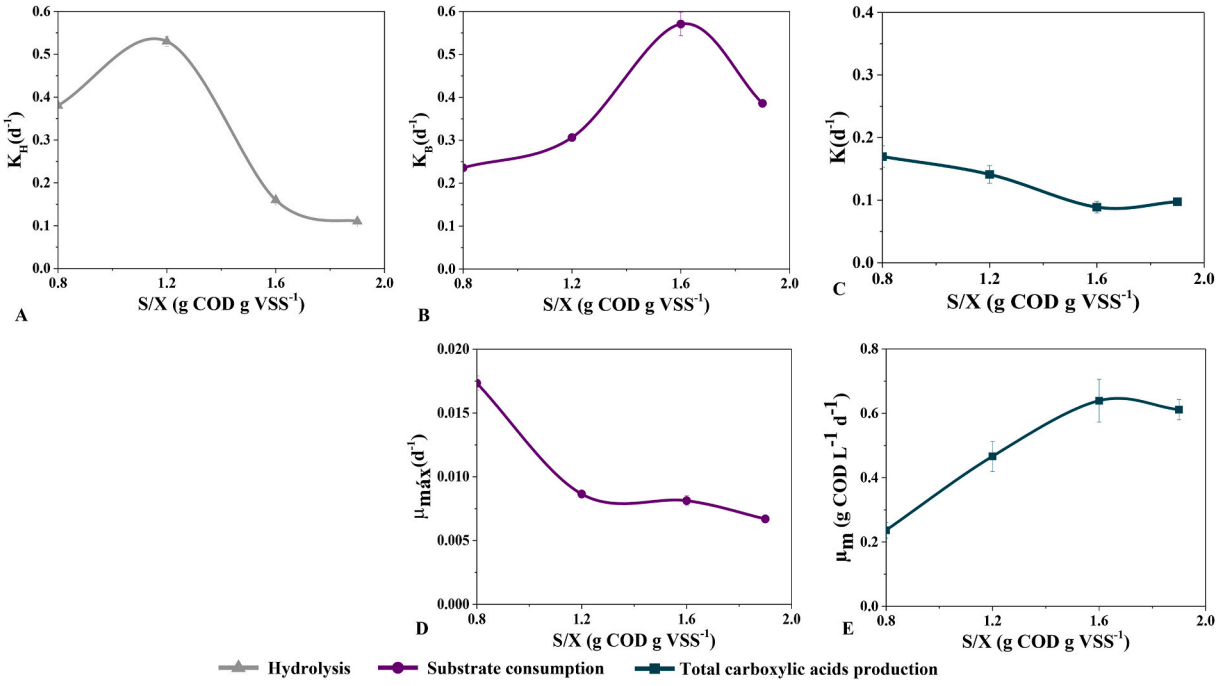

Fig. 4. Correlation of the S/X ratio with hydrolysis rate constant (k_H) (A), soluble substrate consumption rate constant (k_B) (B), carboxylic acids production rate constant (K) (C), maximum microbial growth rate (μ_{max}) (D), and maximum carboxylic acids productivity (μ_m) (E) from the acidogenic batch assays using dairy wastewater as substrate.

conversions of one carboxylic acid into another occurring by several metabolic pathways. Propionic and butyric acids are converted to acetic acid under low hydrogen partial pressure through the β-oxidation route (oxidative pathway), but the acetic acid could be converted into butyric acid through the β-oxidation reverse route (reductive pathway) (Hassan and Nelson, 2012). This rapid acidification was probably due to the presence of readily biodegradable components of DW, mainly lactose (Chwialkowska et al., 2019).

3.2. Kinetic modeling

Process modeling methods are widely used to control and predict the performance of anaerobic treatment systems (Ebrahimi et al., 2018). Such models are mature for the anaerobic digestion focusing on methanization (Çetinkaya and Yetilmezsoy, 2019). However, the kinetic modeling of CA formation from DW at different S/X ratios was not yet reported in the literature.

Among the different mathematical models used to describe kinetics, exponential models, such as First-order with Residual (Fig. 3A–H), were more suitable to describe the hydrolysis and soluble substrate consumption process, with a high coefficient of determinations (R^2) and low values for AIC (Table S3). Such behavior was because the organic matter conversion occurs quickly, different from that described by an elongated S-shaped curve. In this case, there was a continuous availability of soluble organic matter and further production of CA over time (Abdullah et al., 2016; Morais et al., 2019).

The hydrolysis rate constant (K_H), which represents the hydrolysis velocity, showed to be influenced by the S/X ratio (Fig. 4A), being the hydrolytic kinetic more favored in the small S/X ratios (0.8 and 1.2). For the highest S/X ratios tested (1.6 and 1.9), likely an inhibitory effect was more pronounced for hydrolytic microorganisms due to the higher concentration of complex substrate present. The correlation of the S/X ratio can be described by the second-degree polynomial equation $y = -1.24 \times ^2 + 2.94x - 1.46$ in S/X ratios from 0.8 to 1.6 ($R^2 = 0.999$), then there was a discrete reduction of K_H to S/X ratio 1.9. The soluble substrate degradation rate constant (K_B) also was influenced by the S/X ratio (Fig. 4B), being the kinetics more favored in the highest S/X ratios (1.6 and 1.9). There was a positive correlation between K_B and S/X ratio described by the exponential equation $y = 0.21 + 0.002^{3.3x}$ in S/X ratios from 0.7 to 1.5 ($R^2 = 0.999$), then K_B decreases to S/X ratio 1.9. So, the hydrolysis was the limiting step to the highest S/X ratios tested. The rate of particulate organic matter degradation was lower than the rate of consumption of soluble organic matter, i.e., $k_H < k_B$ (Coelho et al., 2020).

Analyzing the kinetics of CA production, exponential models were also better suited to describe this production, such as Fitzhugh models (Fig. 3I-L) that presented the highest coefficient of determination (R^2) and the lowest values for AIC (Table S3). Fig. 4C shows the correlation between the S/X ratio and the CA production rate constant (K_{CA}) estimated by the Fitzhugh model, which can be described by the allometric equation $y = 0.15x^{-0.71}$ ($R^2 = 0.889$). It is important to note that among the studied S/X ratios, the relation of 0.8 was the most favorable kinetic condition for the formation of total CA. On the other hand, the correlation between the S/X ratio and maximum CA productivity (μ_m) estimated by the Transference model (Fig. 4E) showed that μ_m increased with the S/X ratio, being the maximum carboxylic acids productivity achieved at 1.6 ratio. It correlates as opposed to K_{CA}, which can be described by the exponential equation $y = 0.66–2.66^{-2.3x}$ ($R^2 = 0.968$). Furthermore, there was no lag phase for any S/X ratio, according to the factor n of the Fitzhugh model ($n < 1$). This result could be confirmed by sigmoidal models such as Monomolecular and Transference that showed the kinetic parameter $\lambda = 0$, indicating good microbial affinity by the soluble substrate (Morais et al., 2019).

Another important kinetic parameter is the maximum microbial growth rate (μ_{max}), estimated using the Transference model. The values were low for all experiments, decreasing with the S/X ratio increase (Fig. 4D). The μ_{max} showed a decreasing behavior similar to that of the CA formation rate, which is entirely plausible because a lower maximum growth rate of microorganisms can generate a reduction in the velocity of products' formation (Mu et al., 2007).

Regarding the kinetics of individual CAs (Table S4), the formations of HAc, HPr, and HBu were better described by exponential models, such as Cone and First-order. The remaining acids were not modeled individually due to their low production or no detection. Analyzing the mathematical models that best described the CA production curves, it can be seen that the variation in the S/X ratio did not have a significant influence on the velocity constant (K) of the HAc formation. This was based on the fact that for the maximum productivity rate (μ_m), there was an increase with S/X ratio increment, even though no significant difference between 0.8 and 1.2 ratios was found. About HPr, there was a significant reduction in K-value for S/X 1.9, with no significant difference between the other ratios. For the parameter μ_m, there was an increase with the increment in the S/X ratio. For HBu, K enhanced with S/X ratio increase from 0.8 to 1.2, but decreased for the other ratios, while μ_m tripled with the increase in S/X ratio from 1.2 to 1.6, with no significant difference between 0.8-1.2 and 1.6–1.9. Considering all acids analyzed, only HBu showed a small lag phase (λ) that was at most 0.13 day for the S/X ratio 1.6.

It is essential to highlight that at the beginning of the process probably the reductive pathway that leads to the production of HPr and HBu prevails, reaching its maximum productivity in the first two days, after which they start to be transformed into HAc (predominance of the oxidative pathway) (Bastidas-Oyanedel et al., 2015; Hassan and Nelson, 2012). Therefore, according to the estimated kinetic parameters, the S/X ratio 1.6 was more suitable for CA production from acidogenic fermentation of dairy wastewater in the conditions used in this study due to the highest production of carboxylic acids. However, it is necessary to stop the fermentation already after the maximum productivity to avoid deoxidation of the larger chain carboxylic acids or study ways to further promote the chain elongation process in order to obtain medium-chain CA such as caproic acid or even long-chain CA, which have a higher commercial value (Angenent et al., 2016). Besides, the lag phases for forming these acids were extremely short, indicating that the microorganisms quickly transform the DW into CA.

4. Conclusions

The S/X ratio did not influence the percentage of DW conversion into carboxylic acids (42–44%) but affected productivity positively. Acetic acid was the CA formed in the highest concentration for all experiments, followed by propionic and butyric acids. Exponential models were better suited to describe this kinetics process, with high R^2 (0.904–0.999) and low values for AIC (−69.82 – 0.049). Therefore, according to the estimated kinetic parameters, the S/X ratio 1.6 was more suitable for CA production from acidogenic fermentation of dairy wastewater, in which the concentrations of longer CA, i.e., with a higher number of carbons, such as propionate and butyrate, were formed in higher quantities.

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.

Acknowledgments

The authors would like to acknowledge the following Brazilian institutions' support: CNPq, Capes, Fapemig, and INCT Sustainable Sewage Treatment Plants.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2021.117605.

Credit author statement

Amanda de Sousa e Silva, Conceptualization, Investigation, Formal analysis, Writing, Tasso Jorge Tavares Ferreira, Investigation, Naassom Wagner Sales Morais, Conceptualization, Investigation, Formal analysis, Writing, Erlon Lopes Pereira, Supervision, Conceptualization, Investigation, Formal analysis, Writing, André Bezerra dos Santos, Supervision, Conceptualization, Investigation, Formal analysis, Writing.

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