Environmental Technology & Innovation 28 (2022) 102587

Contents lists available at ScienceDirect

Environmental Technology & Innovation

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

Enhancing the recovery of volatile fatty acids from strawberry extrudate through anaerobic fermentation at different pH values

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ARTICLE INFO

Article history:
Received 4 November 2021
Received in revised form 9 February 2022
Accepted 18 April 2022
Available online 25 April 2022

Keywords:
Strawberry extrudate
Volatile fatty acids
Anaerobic digestion
Fermentation
Methane

ABSTRACT

Strawberry extrudate (SE) is a by-product derived from the elaboration of strawberry-tasted products. Adequate management of this substrate would entail a new source of benefit for the berry sector, instead of a costly waste to be treated. The aim of this work is to assess the potential use of SE as a carbon soured for volatile fatty acids (VFA) production through anaerobic fermentation at controlled pH (5, and 9) and without pH control (operational pH around 7). Anaerobic digestion at pH 7 resulted in a negligible accumulation of VFA, being mainly degraded to methane. The operation at the other pHs resulted in a marked drop in methane production and, thus, the accumulation of VFA. At pH 9, around 50% of the fed COD_{tot} (total chemical oxygen demand) was accumulated as VFA. Acetic acid represented 61% of these total VFA. The operation at pH 5 resulted in a lower VFA accumulation, i.e. 15% fed COD_{tot}, although the VFA profile was more complex than at pH 9. Propionic and butyric acids represented 43% and 32%, respectively, of the total VFA accumulated at pH 5.

1. Introduction

Anaerobic digestion has been widely proposed for solid waste treatment in biorefineries thanks to its high treatment capacity and the possibility of obtaining bio-energy through the production of methane (Fermoso et al., 2018). However, obtaining other by-products aside from methane is gaining attention. Volatile fatty acids (VFA) are short-chain fatty acids being produced as intermediate products in the anaerobic digestion process (Bruni et al., 2021; Kleerebezem et al., 2015).

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https://doi.org/10.1016/j.eti.2022.102587

Although VFA generally present a wide range of applications for the industry, their market value depends on the specific compound, but in general, it increases as the number of carbons increase. In that sense, market prices of different VFA follow an order of butyric acid (US$2163/tonne) > propionic acid (US$2000/tonne) > acetic acid (US$600/tonne) (Atasoy et al., 2018; Calt, 2015). These values are much higher than the economic value of methane, i.e. around US$ 0.71/tonne (Eraky et al., 2021; Zhao et al., 2018). VFA are used in a wide range of applications, such as in the production of bioplastics, food, pharmaceuticals, textiles, bioenergy, and cosmetics (Bhatia and Yang, 2017; Mengmeng et al., 2009; Valentino et al., 2017).

Production of VFA through anaerobic digestion has been extensively proposed by utilizing a different range of raw materials as carbon sources, such as glucose, xylose, glycerol, and others (Mockaitis et al., 2020; Rodriguez-Perez et al., 2018). As an alternative to the use of commodity chemicals, studies are currently focusing on the use of less costly raw materials such as lignocellulosic and waste biomasses for VFA production (Lee et al., 2014; Rodriguez-Perez et al., 2018). In this sense, a suitable raw material for VFA production could be the strawberry extrudate (SE). SE is a waste fraction composed of the fibrous part and the achenes present in the strawberry (*Fragaria* × *ananassa*) during the industrial process for obtaining strawberry concentrate (Siles et al., 2013). The worldwide strawberry production has exceeded 8 million tons in 2019 (FAO, 2021), of which about 21% is destined to the elaboration of secondary products based on the strawberry concentrate, like marmalade, yogurt, and flavourings (Rodríguez-Gutiérrez et al., 2019; Serrano et al., 2014). SE can reach up to 7% of the manufactured strawberry weight (Gutiérrez et al., 2017; Pollard et al., 2006). Despite the generated volume, SE has a high organic load and environmental polluting potential, making proper management necessary for its final disposal (Siles et al., 2013). Therefore, the production of VFA through anaerobic digestion could convert SE into valuable products instead of a waste to be treated.

Obtaining VFA through anaerobic digestion requires the control of the hydrolytic and acidogenic steps to enhance the production of more soluble organic compounds and therefore, the transformation to VFA. At the same time, methanogenesis should be avoided to reduce the transformation of VFA to methane (Momayez et al., 2019; Wu et al., 2016). However, the hydrolytic step during the anaerobic digestion of lignocellulosic residues, such as SE, has been recognized as one of the main challenges for the widespread of lignocellulose based biorefineries (Rodriguez-Perez et al., 2018). This has resulted in extensive research on pre-treatments based on physical, chemical, and biological methods, whose results have shown their effectiveness in enhancing the hydrolysis of these residues, but in some cases with the trade-off of increasing costs or releasing inhibitors such as phenolic compounds (Cubero-Cardoso et al., 2020).

Different operational parameters have been reported to influence the production and accumulation of VFA, e.g., pH, temperature, organic loading rate (OLR), hydraulic retention time, and solid retention time (Khan et al., 2016; Lee et al., 2014; Strazzera et al., 2021; Yu et al., 2021; Zhou et al., 2018). Concerning pH, it has been reported that pH above 8.0 or below 6.0 may promote the production of VFA and, at the same time, inhibit the methanogenesis activity (Atasoy et al., 2018; Li et al., 2021). In several studies it has been observed that pH 9 conditions favoured the VFA accumulation from waste activated sludge (He et al., 2016; Huang et al., 2015; Zhang et al., 2009), whereas for wastewater and food waste, VFA production increased with acidic/neutral conditions (Oktem et al., 2006; Zhang et al., 2005). In another study on olive mill solid waste anaerobic digestion, it was found that the pH of the operation strongly affects the anaerobic system and that different compounds, including VFA or phenols, can be obtained by adjusting the operational pH at acidic or basic conditions (Cabrera et al., 2019). However, the olive mill solid waste is a easily biodegradable, whereas the high lignin content in the achenes and the presence of inhibitory phenolic compounds would compromise the biological solubilization of the SE (Siles et al., 2013).

The aim of this work was the valorization of the strawberry extrudate by optimizing the pH parameter to obtain VFA by anaerobic digestion. To this end, it has been proposed to study the process of anaerobic digestion at operational pH 5, pH 7 and pH 9, comparing both total VFA production and the individual VFA composition.

2. Materials and methods

2.1. Substrate and inoculum

SE was provided by HUDISA S.A. (Huelva, Spain), it was preserved at −20 ºC to avoid any undesirable fermentation or degradation. SE is resulted from the extrusion of strawberry fruit with a twin-screw with 0.5 mm sieves at 65 ºC. The main characteristics of the substrate are shown in Table 1. Inoculum for anaerobic fermentation was anaerobic biomass obtained from a full-scale anaerobic reactor treating waste activated sludge at Seville, Spain (COPERO urban wastewater treatment plant).

2.2. Experimental setup

Fed-batch anaerobic fermentation of the SE was evaluated in duplicates at three different pH conditions, i.e., pH 5, pH 7, and pH 9. 2.0 L glass reactors with 1.7 L working volume were used. The reactors were inoculated with 10 g VS/L of anaerobic inoculum at the beginning of the assay. pH was measured every day and HCl (12 N) or NaOH (6 N) was added for manually adjusting to the selected operational pH, except for the reactor at pH 7 which was not controlled according to Serrano et al. (2020). Reactors were continuously stirred at 300 rpm and kept at a temperature of 35 ± 1 ºC using a

Table 1
Physicochemical characterization of the strawberry extrudate.

pH	3.7 ± 0.1
TS (g/kg)	144.7 ± 4.0
MS (g/kg)	5.3 ± 0.5
VS (g/kg)	139.4 ± 4.4
Humidity (%)	85.5 ± 2.4
COD_{tot} (g O_2/kg)	200.4 ± 6.3
COD_{sol} (g O_2/kg)	47.2 ± 3.1
Total phenols (mg Gallic acid/kg)	2185 ± 64
Total sugars (mg Glucose/kg)	2023 ± 99
Uronic acid (mg Galacturonic acid/kg)	6.28 ± 0.12
Rhamnose (g/kg)	0.11 ± 0.01
Fucose (g/kg)	<D.L.
Arabian (g/kg)	0. 34 ± 0.01
Xylose (g/kg)	0.80 ± 0.02
Mannose (g/kg)	3.68 ± 0.07
Galactose (g/kg)	<D.L.
Glucose (g/kg)	0.22 ± 0.01
Oligosaccharides (g/kg)	5.76 ± 0.73

D.L., detection limit; TS, total solids; MS, mineral solids; VS, volatile solids; COD_{tot}, total chemical oxygen demand; COD_{sol}, soluble chemical oxygen demand.

thermostatic chamber. The volume of methane was measured by liquid displacement in a Boyle–Mariotte flask after CO_2 removal by NaOH 2N. Methane production was expressed at standard temperature and pressure conditions (STP), i.e., 0 °C, 1 atm. The gas measured for pH 7 and pH 9 reactors, after CO_2 removal, was assumed to be methane, whereas in pH 5 reactors it cannot be assumed to be only methane after the removal of the CO_2 as a significant amount of hydrogen might be also produced at this pH (Tyagi et al., 2014). The produced volume at this pH 5 was considered to be 100% methane, and it was also compared to the case that 100% would be hydrogen.

The reactors were fed in batch mode with 2 g VS/L of SE (VS, total volatile solid). The reactors were fed again once the concentration of COD_{sol} (soluble chemical oxygen demand), which was daily monitored, reached a stable value, i.e. a variation lower than 5% between consecutive days. For the three operational pH values, SE inputs were loaded for 5 weeks at days 4, 11, 18, 26, and 32 during the experiment. The volume was maintained at a constant level by removing the same volume of digestate than the volume fed to the reactors.

2.3. Analytical methods

pH, COD_{tot} (total chemical oxygen demand), COD_{sol} (soluble chemical oxygen demand), TS (total solid), MS (mineral solid), and VS were determined in SE and in the samples taken from the reactors. All the determinations were carried out in accordance with the APHA (APHA, 2017; Rice et al., 2017). To measure the soluble fractions of the samples, samples were centrifuged and microfiltered with 0.45 μm nylon microfilters, in agreement with Rodríguez-Gutiérrez et al. (2019). The total phenol and sugar content were determined with a spectrophotometric method using a spectrophotometer (BIORAD iMark Microplate Reader, USA), similar to Rodríguez-Gutiérrez et al. (2019). VFA were quantified using a Shimadzu GC-2010 gas chromatograph equipped with a 15 m × 4 mm Nukol-silica capillary column and a flame ionization detector (more details are described in Cabrera et al. (2019)).

3. Results and discussion

3.1. Effect of pH on volatile fatty acids and methane accumulation

3.1.1. pH 7 condition

Operation at pH 7 resulted in high solubilization of the fed COD_{tot}, mainly due to the conversion of up to 70% of the fed COD_{tot} into methane (Fig. 1). Most of the fed COD_{sol} was consumed in less than two days, remaining constant around 190 ± 80 mg O_2/L which accounts for around 2% of the fed COD_{tot}. 25% of the fed COD_{tot} was not solubilized, which may belong to the organic matter present in the achenes from SE. Achenes have a high concentration of lignin, whose structure hampers the biological action of the hydrolytic enzymes (Fang et al., 2018; Siles et al., 2013).

The methane yield coefficient was 344 ± 21 L CH_4/kg VS (51 ± 3 L CH_4/kg SE). The high methane yield can be related to the high content of sugars and readily biodegradable compounds of the strawberry extrudate, which can be easily converted into methane (Trujillo-Reyes et al., 2019). Siles et al. (2013), however, described that the anaerobic digestion of strawberry extrudate may be inhibited at loads higher than 1.5 g VS/L, reporting also a more limited methane yield coefficient, i.e. 230 L CH_4/kg VS. This difference could be a consequence of the different inoculum sources in both experiments, since Siles et al. (2013) used a mixed inoculum from the brewery (highly methanogenic) and from a wastewater treatment plant (highly hydrolytic) in a proportion 7:3, whereas in the present study the inoculum was

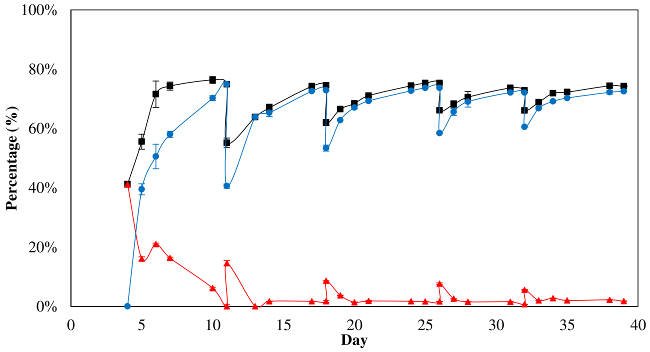

Fig. 1. Solubilization and transformation of SE loaded in pH 7 reactors. (●) Methane, (▲) COD_{sol}, and (■) the sum of (COD_{sol} + Methane) as percentage of fed COD_{tot} against time at pH 7.

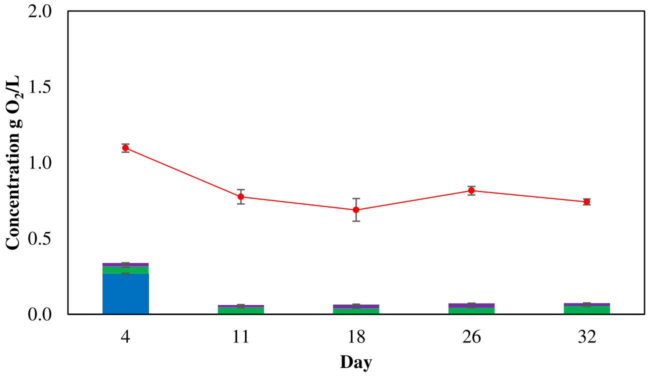

Fig. 2. Solubilization and transformation of SE in COD_{sol} and its distribution in total VFA, sugars, and phenols in reactors without pH control, where 🟦 VFA, 🟩 sugars, 🟪 phenol, and -●- CODsol.

100% from a wastewater treatment plant. The highest proportion of inoculum obtained from a wastewater treatment plant should favour the hydrolysis step, which has been defined as the rate-limiting step in the anaerobic degradation pathway of organic solid wastes (Ortega et al., 2008).

Fig. 2 shows the concentration of VFA, soluble sugars, and soluble phenols determined in the soluble fraction of the reactor effluent of the feeding days. The composition of the soluble fraction of the reactors at pH 7 on the last day of feeding (day 32) was 0.7 g O_2/L COD_{sol}, of which 0.3 g O_2/L corresponded to VFA, 0.05 g O_2/L corresponded to sugars and 0.02 g O_2/L corresponded to phenols. This small accumulation of COD_{sol} was mainly consumed in the following two days (Fig. 1). The accumulation of VFA was minimal in the feeding days (Fig. 2), due to the prevalence of methanogenic activity over the previous metabolic steps (Raposo et al., 2006).

3.1.2. pH 5 condition

In reactors operating at pH 5, solubilization was markedly lower than that obtained at pH 7. Accumulation of both COD_{sol} and methane production by the end of each load, corresponding to an average transformation of 55% of the fed COD_{tot} (33% of the fed COD_{tot} in case all generated volume would be hydrogen), indicating that the hydrolysis was maintained almost constant throughout the experimental time regardless biogas production. On one hand, considering that all measured biogas volume was methane, the methanization increased with the experimental time from 10% to 35% of the fed COD_{tot}. On the other hand, if all measured biogas volume was considered as hydrogen, hydrogen production at the end of each load reached around 18% of fed COD_{tot}. Together with the increased biogas production, it was observed that COD_{sol} during the operation decreased from 50% to 20% of the fed COD_{tot} (Fig. 3).

The decrease in the methane yield coefficient at pH 5 with respect to pH 7, i.e. 28 ± 2 L CH_4/kg VS and 189 ± 12 L CH_4/kg VS, showed that the methanogenic activity was strongly affected at pH 5 favouring the accumulation of VFA (Fig. 3). The same behaviour when decreasing the operational pH from 7 to 5, was previously described by Cabrera et al. (2019) for the anaerobic fermentation of olive mill solid waste and by Serrano et al. (2020) for strawberry waste.

Fig. 4 shows the concentration of COD_{sol}, VFA, soluble sugars, and soluble phenols at the end of each load. The sum of VFA, sugars, and phenols at day 32 reached up to 78% of the COD_{sol} in the reactor. The concentration of VFA increased at each load, reaching maximum values of 1.99 ± 0.05 g VFA-O_2/L at the end of the experiments, similarly Cabrera et al.

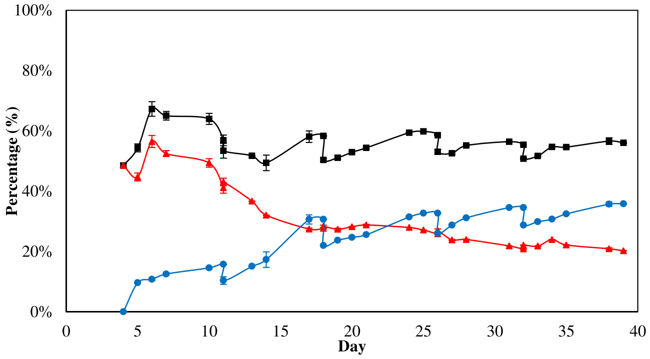

Fig. 3. Solubilization and transformation of SE loaded in pH 5 reactors. (●) Methane, (▲) COD_{sol}, and (■) the sum of (COD_{sol} + Methane) as percentage of fed COD_{tot} against time at pH 5.

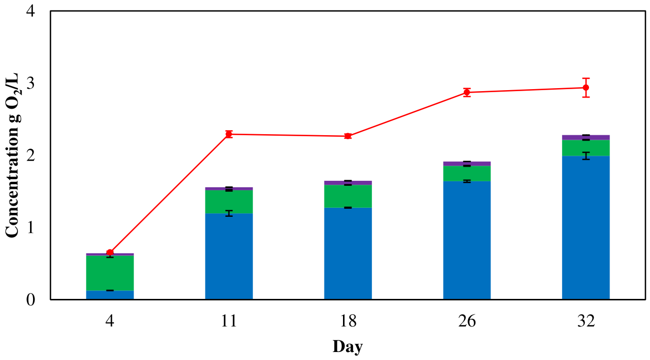

Fig. 4. Solubilization and transformation of SE in COD_{sol} and its distribution in total VFA, sugar and phenol in reactors at pH 5, where 🟦 VFA, 🟩 sugars, 🟪 phenol, and -●- CODsol.

(2019) obtained 1.69 g VFA-O_2/L from olive mill solid waste at pH 5. Soluble sugars were decreasing during reactor operation, reaching the lowest value of 0.22 ± 0.01 g O_2/L after the last load on day 32. The concentration of soluble phenols observed at the end of each load was almost constant, reaching a mean value of 0.07 ± 0.01 g O_2/L.

The operation at pH 5 clearly favoured the accumulation of VFA respect the operation at pH 7. Recent studies have demonstrated that the operation at pH 4 resulted in the total inhibition of the methanogenesis during the anaerobic fermentation of wasted strawberries (Serrano et al., 2020). However, these authors also reported that the operation at pH 4 affected the acidogenic activity, resulting in a poor accumulation of VFA, i.e. the average VFA/COD_{sol} ratio was 0.17 ± 0.07 (Serrano et al., 2020).

3.1.3. pH 9 condition

The operation at pH 9 resulted in the total inhibition of methane production (Fig. 5). The inhibition of the anaerobic digestion can be explained by the sensibility of the methanogens to alkaline operation conditions (Li et al., 2018). Alkaline conditions also favour the solubilization of the extracellular polymeric substances, enhancing the accumulation of COD_{sol} (Lee et al., 2014; Li et al., 2018). Throughout the operation it was observed that COD_{sol} decreased from 90% to 50% of the fed COD_{tot} (Fig. 5). pH 9 reactors showed more than double COD_{sol} accumulation that at pH 5 during the operation, despite the slightly lower hydrolysis. Total inhibition of the methanogenic activity was the key factor for improving the accumulation of VFA during the operation at pH 9.

Fig. 6 shows the concentration of COD_{sol}, VFA, soluble sugars, and soluble phenols throughout the experimental time. The sum of VFA, sugars, and phenols on 32 days reached 100% of the COD_{sol}. Specifically, the 100% COD_{sol} composition showed a mean distribution of 95%, 4%, and 1% for VFA, soluble sugars, and soluble phenols, respectively, at the end of the operation. The accumulation of VFA increased at the end of each load, reaching a maximum value of 6.18 ± 0.01 g O_2/L, three times higher than at pH 5. In contrast, the concentration of soluble sugars decreased at each load, reaching minimum values of 0.25 ± 0.01 g O_2/L at the end of the experiments. The concentration of soluble phenols remained almost constant, with a mean value of 0.07 ± 0.01 g O_2/L.

It was observed that the VFA were the main components of COD_{sol}, showing that acidogenesis was not affected by the alkaline conditions (Chen et al., 2007; Serrano et al., 2020). However, similar to pH 5, hydrolysis was strongly affected at pH 9, as both COD_{sol} and methane production reached around 50% of COD_{tot}, whereas at pH 7 reached around 75%.

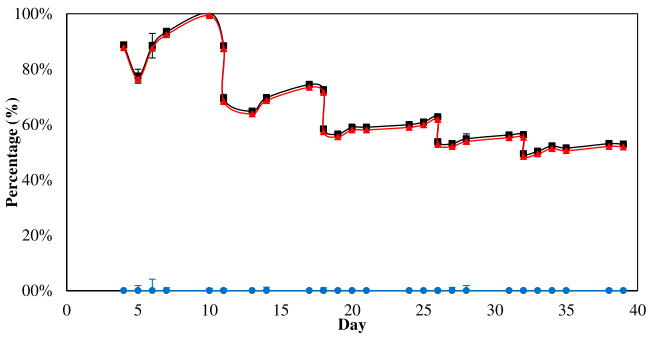

Fig. 5. Solubilization and transformation of SE loaded in pH 9 reactors. (●) Methane, (▲) COD_{sol} and (■) the sum of (COD_{sol} + Methane) as percentage of fed COD_{tot} against time at pH 9.

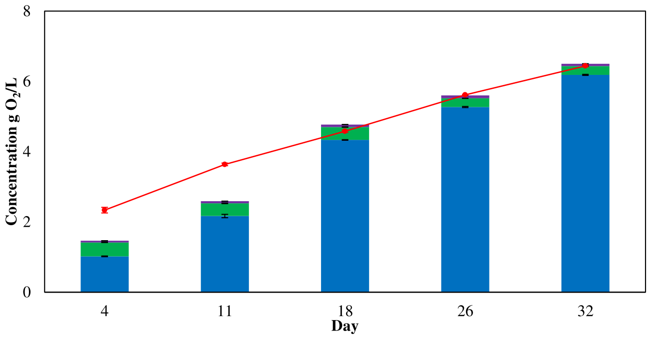

Fig. 6. Concentration of COD_{sol} and its distribution as total VFA, sugar and phenol in reactors at pH 9, where 🟦 VFA, 🟩 sugars, 🟪 phenol, and -●- CODsol.

3.2. Individual VFA profiles at each operational pH

Fig. 7 shows individual VFA produced in pH 5, 7, and 9 reactors. As expected, the high methane yield achieved during the operation at pH 7 resulted in the almost complete degradation of the VFA at the end of each load (Figs. 1 and 7). Therefore, only minimal concentrations of propionic and acetic acid were detected on the day after each load, to be rapidly degraded to methane during the subsequent days (Fig. 7).

At the end of the experimental time in the pH 5 reactor, the distribution of VFA was 43% propionic acid, 32% butyric acid, 7% iso-valeric acid, 7% valeric acid, 5% iso-butyric acid, 4% caproic acid, and 2% acetic acid (Fig. 7). From the first load of SE, propionic acid and butyric acid started being accumulated (Fig. 7). Propionic acid was the main accumulated VFA, reaching a maximum of 605 mg/L (0.914 g COD/L from VFA). The accumulation of propionic acid as the main VFA at acid pH was previously described by different authors (Darwin et al., 2018; Serrano et al., 2020). At the same time, acetic acid tended to be accumulated in the first days after the load, to then decrease in the last days, in line with the increase of methane production (Fig. 7). It has been observed in different studies that in substrates with a high carbohydrate content, as SE (Table 1), a low amount of acetic acid and a higher amount of propionic and butyric acids were produced at acid pH as in this study (Dahiya et al., 2015; Strazzera et al., 2018). The diversity of VFA in pH 5 reactors could be due to the fact that the activity of acetoclastic methanogens and propionic and/or butyric oxidizing bacteria decreased (Cabrera et al., 2019).

In the pH 9 reactor, the acetic acid was clearly the main component of the total VFA, reaching a maximum concentration of 3950 mg/L (4.02 g COD/L from VFA) at the end of the experimental time (Fig. 7). Propionic acid was the second with the highest concentration, i.e., 725 mg/L (1.10 g COD/L from VFA), reaching a concentration similar to that obtained at pH 5. The percentage of acetic acid from total VFA increased from 40 to 60% until the end of the operation. The preponderance of the acetic acid indicated that at pH 9, in contrast to the results obtained at pH 5, the acetogenesis activity was not affected, whereas the methanogenic activity was effectively inhibited. The percentage of propionic acid from total VFA was constant over time, around 16%–18% (Fig. 7). The decrease in methanogenic activity could also be due to the high concentration of propionic acid since the reached concentration was close to the inhibition limit described by Wang et al. (2009), i.e. 900 mg propionic acid/L. The distribution of acids in the reactors at the end of the last load indicated the high preponderance of acetic acid and, to a lesser extent, propionic acid, whereas the other measured acids represented a minimal percentage of the total VFA, i.e., 61% acetic acid, 16% propionic acid, 7% iso-valeric acid, 5% iso-butyric acid, 4% butyric acid, 4% caproic acid, and 3% valeric acid. It has been as well reported by other authors that at pH 9 acetic acid

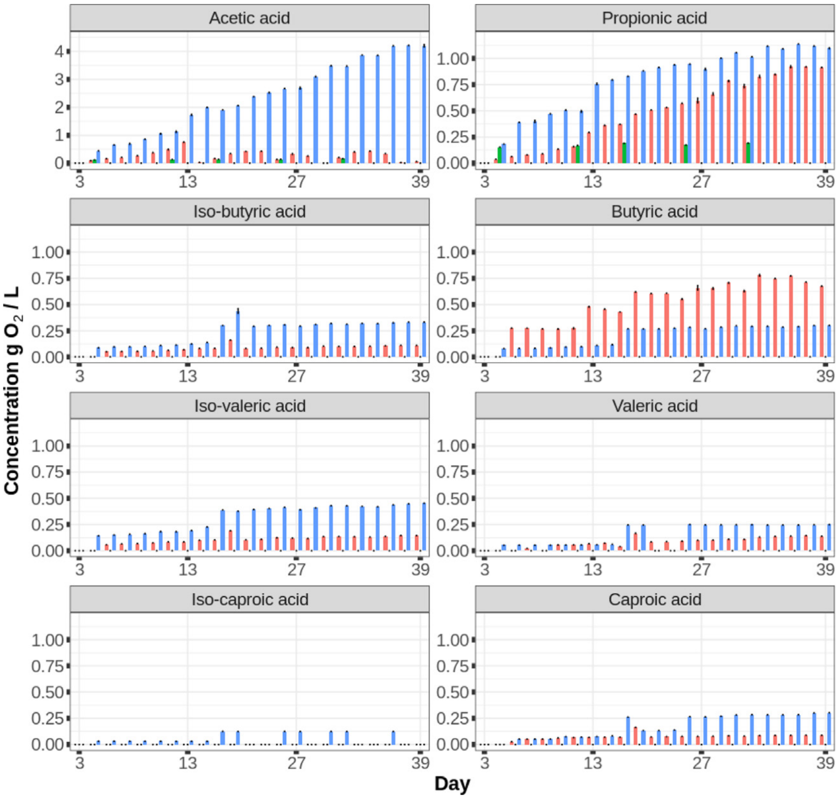

Fig. 7. Characterization of individual volatile fatty acids produced in pH 5, 7 and 9 reactors, where 🟥 pH 5, 🟩 pH 7, and 🟦 pH 9.

is the most abundant in comparison with the rest of VFA (Dahiya et al., 2015; Garcia-Aguirre et al., 2017; Manuel et al., 2021; Strazzera et al., 2018). It has also been also previously reported that at pH 9 there is a higher concentration of VFA compared to acidic pH, probably as at alkaline conditions carbohydrates are easier to solubilize than at acidic conditions (Dahiya and Mohan, 2018; Strazzera et al., 2018).

4. Conclusions

The operational pH during the anaerobic fermentation of the SE was a crucial factor influencing both the concentration and the composition of the accumulated VFA. At pH 7, the anaerobic microorganisms degraded around 70% of the fed organic matter into methane. On the contrary, pH 5 and 9 strongly restricted the methanogenic activity, allowing the accumulation of VFA. At pH 9, up to 50% of the fed COD_{tot} was converted into VFA, mainly as acetic acid. The operation at pH 5 resulted in a more limited conversion into VFA, i.e., only 15% of the fed COD_{tot} was converted into VFA. However, the VFA profile at pH 5 was more complex than at pH 9, being propionic and butyric acids the main components of the VFA. Although the operational pH can be a crucial factor for controlling the concentration and composition of the accumulated VFA, further research would be still necessary for improving the hydrolysis of the SE under no neutral pH.

CRediT authorship contribution statement

Juan Cubero-Cardoso: Methodology, Formal analysis, Writing – original draft. **Egidio Russo:** Methodology, Investigation. **Antonio Serrano:** Formal analysis, Writing – review & editing. **Ángeles Trujillo-Reyes:** Methodology, Formal analysis, Writing – original draft. **Denys Villa-Gomez:** Data curation, Validation. **Giovanni Esposito:** Supervision, Writing – review & editing. **Fernando G. Fermoso:** Supervision, Conceptualization, Methodology, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Fernando G. Fermoso reports financial support was provided by Spanish Ministry of Economy and Competitiveness. Antonio Serrano reports financial support was provided by Spanish Ministry of Science, Innovation,

and Universities and the Economic Transformation, Industry, Knowledge and Universities Department of the Andalucia Autonomous Government. Juan Cubero-Cardoso reports financial support was provided by Regional Government of Andalusia, Junta de Andalucía, Consejería de Economía y Conocimiento.

Acknowledgements

The authors are very grateful to the Spanish Ministry of Science and Innovation for funding this research through the project PID2020-116698RB-100. Antonio Serrano is grateful to the Spanish Ministry of Science, Innovation, and Universities for his Juan de la Cierva-Incorporación fellowship (IJC2019-040933-I) and to the Economic Transformation, Industry, Knowledge and Universities Department of the Andalucia Autonomous Government for his Emergia fellowship (EMERGIA20_00114). The authors are grateful to the Regional Government of Andalusia, Junta de Andalucía, Consejería de Economía *y* Conocimiento (Project UHU-1257728), for providing additional financial support. Funding for open access charge: Universidad de Granada/CBUA. The authors also wish to express their gratitude to Javier Ramiro-Garcia and Ainoa Botana Samper for their assistance with this research.

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