Significant volatile fatty acids production by using primary and digested sludge as raw materials in anaerobic fermentation

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Abstract

The use of waste as a renewable raw material is highly studied for development of next-generation technologies to produce fuels, chemicals, and materials; and one of the main waste stream generated worldwide causing environmental impacts due to its lack of management is the sludge from wastewater treatment plants, which can be valued as volatile fatty acids (VFA). Therefore, the present study explored the production of VFA from primary and digested sludge by the evaluation of different operative conditions in an anaerobic fermentation process. The experimental design managed three independent variables; organic loading (OL) rate was evaluated in two levels (6 gVS/L and 4 gVS/L) for primary sludge (PS) and (10gVS/L and 14 gVS/L) for digested sludge (DS), pH values of 9.0, 10.0 and 11.0; this was evaluated under mesophilic conditions, a temperature around 35°C, for both residues. The results showed that the highest total VFA production was accomplished by using primary sludge, with an OL of 14gVS/L, a pH of 11.5 and at 35°C (5496±0.02 mg COD/L at day 6). VFA yield is strongly affected by the pH and the inhibition of methane production. Likewise, the high content of proteins and the OL of the essays performed with PS resulted in significant production of VFA, indicating a strong difference from the DS assays.

Keywords: volatile fatty acids, anaerobic digestion, sludge treatment, bio-based products

Introduction

Bioconversion of waste streams has been set as an opportunity to accomplish environmental sustainability, where the production of value-added products is central to now-days research. Renewable resources have a high demand for the development of next-generation technologies to produce fuels, chemicals, and materials from organic waste streams [1]. Following this, anaerobic digestion has been presented as a processing technology with a major role among the circular economy concept, when it is seen as a platform for the valuation of heterogeneous wastes in resource recovery systems, energy and high-value added products [2]. Indeed, between the anaerobic digestion most known products are: a) methane and bio-fertilisers, as the most traditional and adopted process variation; followed by bio-hydrogen production, dark fermentation variation; and the production of soluble biochemicals, mostly volatile fatty acids (VFA) produced during acidogenesis stage [3].

Volatile fatty acids production from waste streams has been studied for the reduction of cost efficiency problems of the current treatments, also for fuel and materials production, principally, VFAs are considered building blocks for industrial processes and can be used as a carbon source on the production of biopolymers [4, 5]. VFA can be produced by mixed microbial culture anaerobic fermentation of different substrates, where VFA is an intermediate product according to the stages of the process. Therefore, the main conditions for the production of VFA are the assessment of: the reaction time (4 to 15 days); the adjustment of pH values, above 8 and under 6, depending on the substrate; also, temperature, which has been studied from psychrophilic (5–30 °C) to thermophilic (50 to 100°C) conditions [1, 6, 7].

In accordance with this, one of the main waste stream generated worldwide is the sludge from wastewater treatment plants (WWTP), this sludge contains high amounts of organic and inorganic contaminants, along with pathogens, that without correct treatment leads to acute environmental and human health problems [8, 9]. The treatment of wastewater has included anaerobic digestion; although during the last decade, academy has focused on creating opportunities and prospection of biorefinery-based valorisation for WWTP. This has included the production of VFA as raw material for value-added products generation, such as bio-degradable polymers [10, 11]. Consequently, this work investigates the effects of organic load, pH, and temperature as main operative conditions for the anaerobic fermentation of primary and digested sludge from El Salitre WWTP, Bogotá (Colombia).

Materials and methods

Inoculum and raw materials characteristics

The primary sludge and digested sludge used for the anaerobic fermentation were collected at El Salitre WWTP, which is the primary sanitation system of Bogotá (Colombia). The sludge samples were preserved at 4°C to prevent any degradation before the anaerobic fermentation process. The average characteristics of each sludge are as follow: primary sludge, VS (volatile solids) 39.16±0.06 g/L, TS (Total Solids) 52.35±0.07 g/L, TCOD (Total chemical oxygen demand) 142 g/L; digested sludge, VS 11.40±0.08 g/L, TS 52.35±0.12 g/L, COD 125.5 g/L.

Moreover, to support the start-up of the fermentation process, an inoculum was used for the experimental setup; the granular sludge was obtained from the sewage plant of Alpina S.A. in Sopo, Cundinamarca (Colombia), before the essays it was pre-treated by thermal shock [12]. The concentration of VS and TS in the inoculum was 76.07±0.42 and 84.03±0.49 g/L, respectively.

Batch fermentation experimental set up

An experimental design was built to determine the conditions that favor the production of VFA, the experiments where conducted on a laboratory scale. The design managed three independent variables, where the organic load (OL) was differentiated for each type of sludge: OL was evaluated in two levels for digested sludge (DS) (6 gVS/L and 4 gVS/L), and (10gVS/L and 14 gVS/L) for primary sludge (PS), pH values of 9.0, 10.0 and 11.0; a temperature around, 35°C for both residues (see Table 1.). The substrate to inoculum ratio was set as 1:1, in order to reduce the inhibitory effects during the fermentation [13].

There were six (6) combinations for each substrate, and the tests were carried out using batch reactors of 250 mL, hermetically sealed, and placed in a thermostated bath. The reactors were filled with the necessary amount of sludge, inoculum, water, and a buffer solution, to guarantee pH conditions; along with an adjustment with NaOH to the required pH value. Each combination had 12 replicates, monitored by a destructive sampling, set every three days, where the biogas composition was measured using BIOGAS 5000® Landtec and samples were collected for the further quantification of the pH, VFA (mg COD/L), alkalinity (mg $CaCO_3$/L) and COD (mg/L) produced during the reaction time.

Table 1. Experimental design

Combination		**1**	**2**	**3**	**4**	**5**	**6**
OL (gSV/L)			6			4	
Temperature |(°C)	**DS**		35			35	
pH		9	10	11	9	10	11
Combination		**7**	**8**	**9**	**10**	**11**	**12**
OL (gSV/L)			14			10	
Temperature (°C)	**PS**		35			35	
pH		9	10	11	9	10	11

Statistical Methods

According to previous researches, the calculation of the VFA production efficiency results from the total VFA concentration in the effluent per grams of volatile solids (VS) fed (g COD/g VS) [14]. This calculation allowed the assessment of the acidification potential of the substrates, and the further definition of the best operative conditions. Additionally, all the analyses were performed by triplicate for each sample.

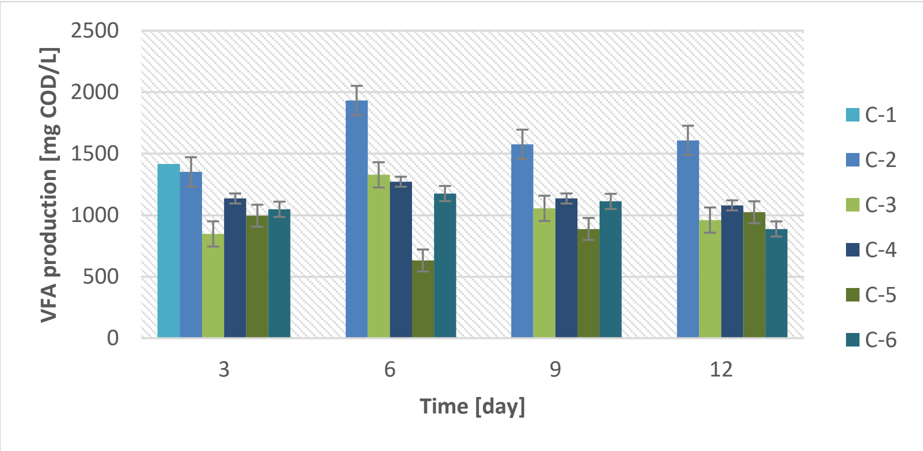
Analytical Methods

Total Solids (TS), Volatile Solids (VS), pH, Kjeldahl Total Nitrogen (KTN), Volatile fatty acids (VFA) and Alkalinity measurements of the initial substrates and the digestate were determined according to America Society for Testing and Materials (ASTM). Measurements of pH were determined using a pH meter Edge model HI2002, following the standard test method D 4972-01 of the ASTM. VFA and Alkalinity where measured according to (APHA, 2005). KTN was determined according to the D1426 of the ASTM. The Soluble Chemical Demand of Oxygen (SCOD) was measured using commercial vials with a range of 0 to 150 mg/L (HI 93752), samples from bioreactors were centrifuged at 6000 rpm for 10 min before the test Finally, the gas composition measurements (CO_2, CH_4 and O_2%) was determined by the gas analyzer BIOGAS 5000® Landtec.

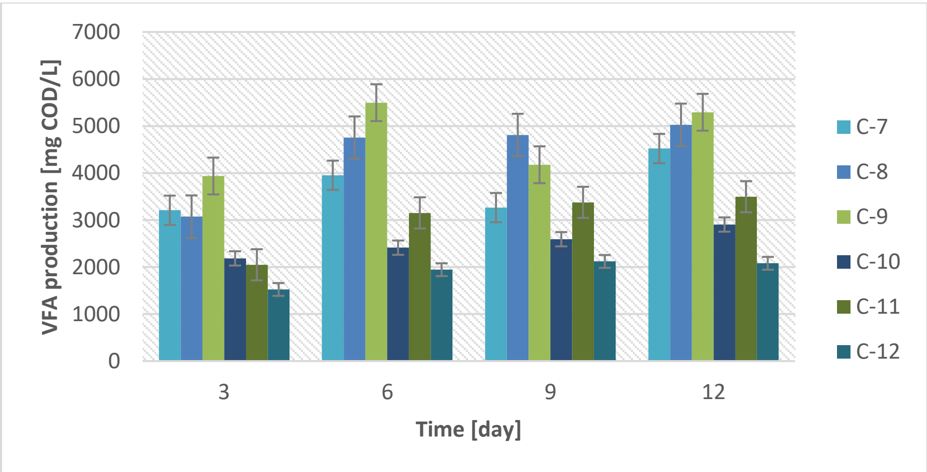
Results and discussion

Reflected in the time-course profile of the batch anaerobic fermentation under the conditions established, the highest total VFA production, from all the current evaluated combinations, was achieved using primary sludge, with an OL of 14 gVS/L and a pH of 11 (5496±0.02 mg COD/L at day 6). Also, for the digested sludge, the highest total VFA production was achieved with an OL of 6 gVS/L and a pH of 10 (1932±0.11 mg COD/L at day 6); see Figure 1. As the experiments were performed as conventional anaerobic fermentation process, the inoculation and pH adjustment were key to prevent methanogens and hence the production of VFA, by stopping the degradation at the acidogenic stage [13, 15]. This is observed in VFA production reported for day 3 (1352±0.06 mg COD/L for C-2 and 3936±0.03 mg COD/L for C-9).

Moreover, the OL has a direct relationship on the VFA accumulation; also, given to the different characteristics of the substrates, the VFA production is affected. The results show that the PS carbon source for VFA production is between a 30 to 44% more feasible. Indeed, the primary sludge includes a greater diversity of compounds, along with different biodegradation characteristics, than in the digested sludge which has been already treated under anaerobic conditions [16]. Similarly, [17], It was identified that due to the excessive content of organic compounds in sewage sludge, they provide a positive potential for the recovery of VFA; though, the composition and properties of the residual digested sludge can limit its biodegradability and hinder the production of VFA [18].



(a)



(b)

Figure 1. VFA production by anaerobic fermentation during a reaction time of 12 days; (a) digested sludge, (b) primary sludge.

Regarding the alkalinity, Figure 2. shows the effect of alkalinity on VFA production. As the initial alkali pH was set to 9, 10 and 11 with no pH control during the experiments, the result showed that the initial pH favoured the hydrolysis of the substrates until pH drops to neutral level, while VFA accumulation was higher. Therefore, regarding the pH levels drop, for the total retention time, the variations were as follows: 7.27 to 8.48 for pH 9; 9.67 to 8.64 for pH 10 and 9.54 to 10.43 for pH 11. As the alkalinity remained high, which may be associated to the buffer capacity of the substrate, the addition of buffer solutions in the beginning of the process and the complexity of the substrate.

In accordance with this, [19], conducted a similar analysis where is shown that alkali pH are major responsible for variability of the VFA production when using complex substrates; where the initial alkaline pH promoted hydrolysis of the organic matter when compared to the acidic conditions.

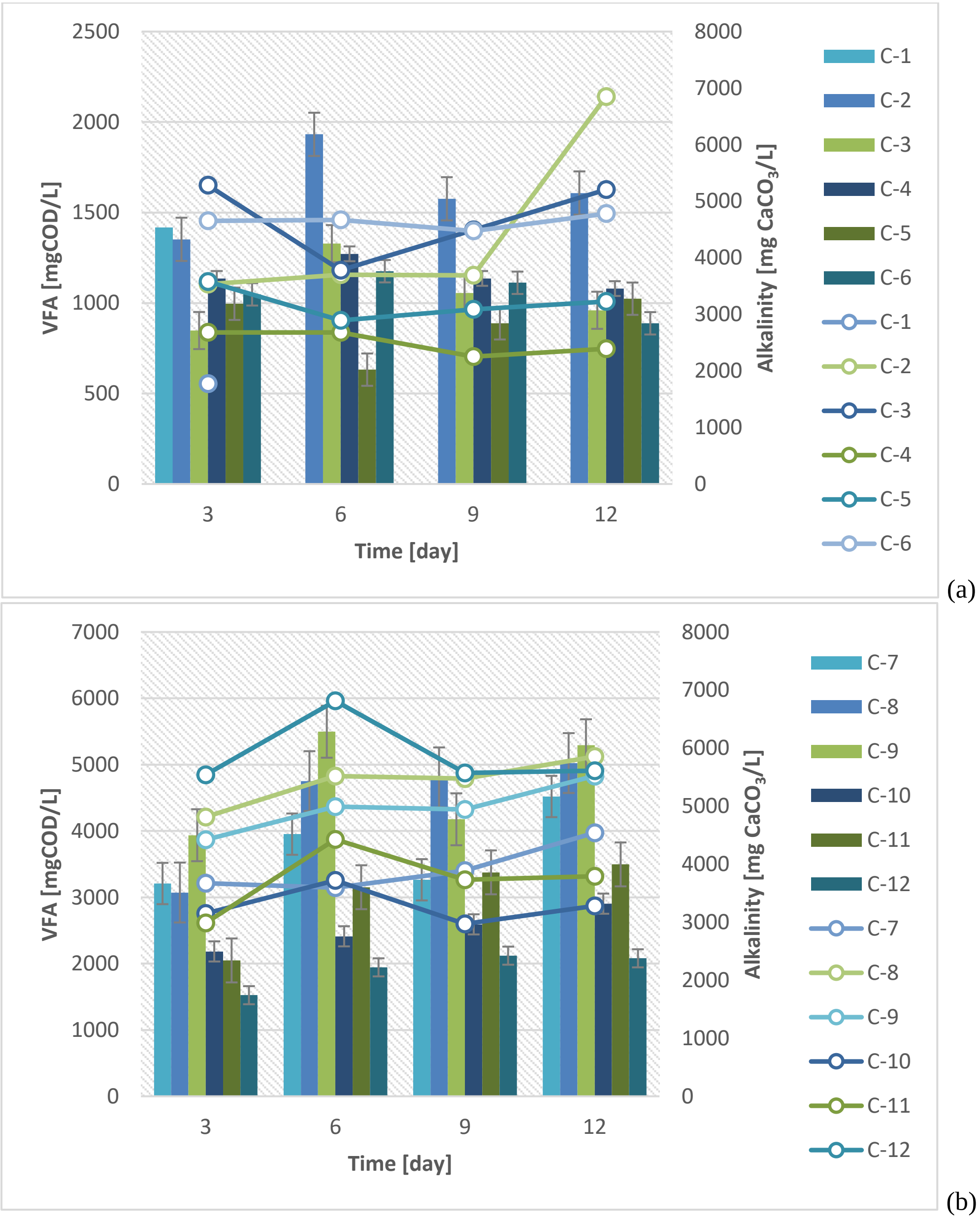
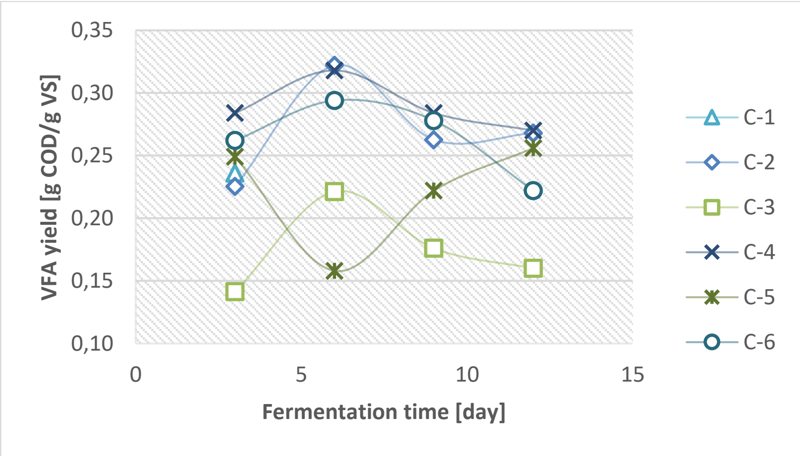


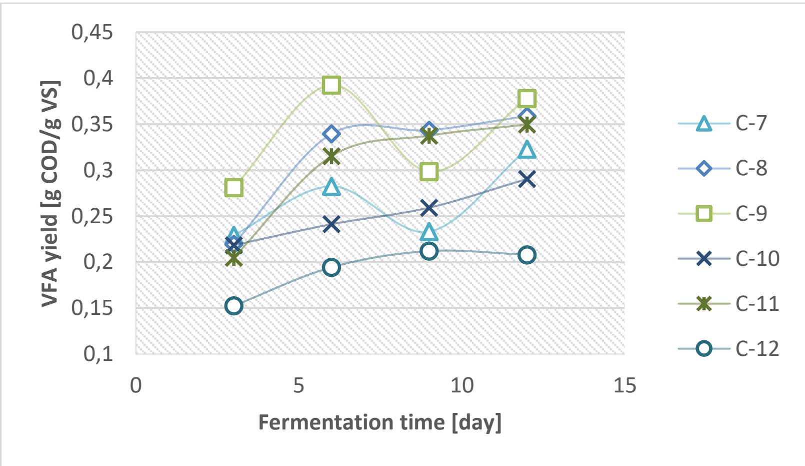
Figure 2. VFA vs alkalinity performance during the anaerobic fermentation for a reaction time of 12 days; (a) digested sludge, (b) primary sludge.

The total VFA yield for the digested sludge, fluctuated from 0.14 to 0.27 (g COD/g VS) for the conditions with 6gVS and from 0.22 to 0.32 (g COD/g VS) for conditions with 4gVS, while; for primary sludge, fluctuated from 0.21 to 0.39 (g COD/g VS) for the conditions with 14gVS and from 0.15 to 0.34 (g COD/g VS) for conditions with 10gVS (see Figure 3). As a staged process, general measurements showed that in most cases, the highest accumulation of VFA were registered during the first days. Although, the VFA yield increases during last days (the case of C-9, with a medium yield of 0.33 g COD/g VS), which suggests that higher pH values enhance the inhibition of the consumption of the produced VFA by methanogens [9, 20]. Furthermore, from the biochemical fermentation process point of view, the main metabolites expected are acetic, propionic and butyric acid; where acetate is the main precursor for CH_4 conversion, between 65 and 95% is produced from acetic acid [21, 22].

The SCOD measured at the end of the experimentation, for the best combination enabled to determine the effect of the pH adjustment on SCOD release and VFA production. In general terms, the SCOD increased with the alkaline pH adjustment by the solubilization of large COD particles (proteins, carbohydrates, and polysaccharides) [23, 24]. As the best yields resulted from the tests with pH 10 at day 12 and 11 at day 6, an enhance on hydrolysis along with a high SCOD was identified (49.6g SCOD/L for C-2 and 67.65g SCOD/L for C-9, at day 3).



(a)



(b)

Figure 3. Anaerobic fermentation performance of primary sludge in terms of the VFA production efficiency for a reaction time of 12 days; (a) C-1, C-2, and C-3 were evaluated for 6 gVS while C-4, C-5, and C-6 were evaluated for 4 gVS; (b) C-7, C-8, and C-9 were evaluated for 14 gVS while C-10, C-11, and C-12 were evaluated for 10 gVS.

It is important to have in mind, that during the evaluation at psychrophilic (5–30 °C) and thermophilic (50 to 100°C) conditions, the biochemical reaction rate could change according to the growth of the microorganisms [25]. Changes on the production and yield of VFA rise at thermophilic temperature, due to the increase on the solubility of carbohydrates and proteins; although this is also attached to the sludge microbial culture adaptation [24, 26, 27].

Conclusions

The results obtained allow the implementation of the most suitable anaerobic fermentation conditions to produce VFA for the further production of renewable value-added products. The highest yield was produced from the fermentation of primary sludge, under an OL of 14 g VS/L, at 35°C and a pH of 11, where the methanogens were inhibited. Likewise, the high content of proteins and the OL of the essays performed with PS resulted in significant production of VFA, strongly differenced from the DS assays. However, it is important to assess under psychrophilic and thermophilic conditions, to establish the operative parameters for the scale-up of the process. On the other hand, the results related to VFAs production using as raw material digested sludge represent an important assessment in order to stablish the potential of this residual biomass to obtain value added products. Following this, the results of this research will be the basis for future research on the production of sustainable-based polyhydroxyalkanoates, through the recovery of municipal wastewater, using VFAs as a substrate.

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