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Volatile Fatty Acids Production from Fermentation of Waste Activated Sludge

Jeniffer Gracia[ab], Jhessica Mosquera[c,d], Carlos Montenegro[b], Paola Acevedo[ac], Ivan Cabeza[d]

[a]Department of Industrial Engineering, Universidad Cooperativa de Colombia, Bogotá, Avenida Caracas 37-63, Colombia
[b]Universidad Distrital “Francisco José de Caldas”, Bogotá, Carrera 7 No. 40B-53, Colombia
[c]Facultad de Ingeniería Ambiental, Universidad Santo Tomás, Bogotá, Carrera 9 No 51-1, Colombia
[d]Facultad de Ingeniería, Diseño e Innovación, Politécnico Grancolombiano, Bogotá, Calle 57 No. 3-00 Este, Colombia
jeniffer.gracia@campusucc.edu.co

The population growth has increased in the globe and, with it, the waste generation resulting in a severe problem. It is mandatory to assess production alternatives for the generation of bio-based products from residual sources. As is well known, plastic pollution is one of the main issues, one of the alternatives to overcome the unstoppable demand for this product are bioplastics derived from polymers of biological origin. One of the main steps for the synthesis of the biopolymers is the volatile fatty acids (VFA) production by anaerobic digestion of residual sources. Consequently, this work evaluates the production of VFA by anaerobic digestion of activated sludge from a municipal wastewater treatment plant. An experimental design was constructed to determine the conditions that favour the production of VFA. The design managed three independent variables: the organic load (6 gVS/L and 4 gVS/L), pH values of 9.0, 10.0 and 11.0, and a temperature of 25°C. The results of the study show that the activated sludge is suitable to produce VFA, due to the total concentration; also it may be used as carbon source for bio-polymers synthesis in future stages of the process. Alkaline conditions seem to boost the production of VFA, which was between 372 to 1600 mg COD/L.

1. Introduction

Solid waste generation rates are rising fast around the globe, due to the population growth, which also has led the researches on alternatives for the treatment and production of bio-products from valorisation of waste. Wastes that are not only an environmental problem, but also an economic loss. Value-added bio-based products can be obtained from different types of organic waste (Liguori, et al., 2013), where some of the main products are bio-fuels and bio-plastics. Bioplastics derived from polymers of biological origin provide a solution to the growing problem of the management of different types of waste, such as activated sludge derived from the wastewater treatment industry. Activated sludge has a great potential to produce volatile fatty acids (VFA) that act effectively as a carbon source for the growth of microorganisms for the synthesis of biopolymers (Kumar et al., 2019). Volatile Fatty Acids, can be generated by the anaerobic fermentation of biodegradable waste. During fermentation, the group of microorganisms responsible for the VFA production are known as acetogenic bacteria and homoacetogenic bacteria, in the acidogenesis process (Yuan et al., 2019). The fermentation process implies the generation of hydrogen and VFAs (acetic, propionic, butyric and valeric acid, principally) (Khan et al., 2016). According with previous researches, the extraction of VFA depends on several operative conditions, in consonance with the metabolic pathway wished to enhance the production; including: reactor type, design, substrate composition and product spectrum; apart from temperature, pH, retention time and organic loading rate, which will depend on the previous established conditions (Khan et al., 2016; Strazzera et al., 2018). The optimization on the production of VFA will favour its future use as carbon resource on the production of polyhydroxyalkanoates (PHA) and the production of bio-fuels like hydrogen and methane gas. Currently, this biochemical process is used worldwide to stabilize municipal sludge, to treat industrial waters and for the digestion of organic waste, by using the bacterial cultures of wastewater and solid waste,

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the environmental impact of those sources of pollution is reduced and also the production costs of bio-based products is lowered (Luo et al., 2019). This type of system also offers cost-effective solutions for the transformation of complex substrates into stable products that may have an industrial value such as hydrogen and methane (Jaramillo, 2016). In this way, the present work is focused on the evaluation of the potential of activated sludge to produce VFA under different conditions for the further optimization of the process.

2. Methodology

2.1 Inoculum and waste activated sludge

To guaranty the startup of the testing, methanogenic granular sludge was used for the experimental set up, the inoculum was obtained from the sewage plant of Alpina S.A. in Sopo, Cundinamarca (Colombia), where a stabilized anaerobic reactor manages waste water from the industrial process. A heat shock treatment was necessary for an acidogenic fermentation system, the inoculum was boiled during 30 min and let to cool down till ambient temperature before to be added to each of the reactors (Hernández et al., 2018).
The waste activated sludge (WAS) was collected from El Salitre waste water treatment plant (WWTP), that is the main plant of this kind in the city of Bogota (Colombia), WAS main physicochemical characteristic are showed in Table 1. The WAS was kept in a freezer at -4°C to avoid the microbiological degradation before the tests.

Table 1: Physicochemical characteristics of inoculum and waste activated sludge

	Total solids (TS)[b]	Organic matter (OM)[a]	Volatile solids (VS)[b]	Total Kjeldahl nitrogen (TKN)[b]	Chemical oxygen demand (COD)[b]
WAS*	3.09±0.01	54.74±0.01	1.69±0.41	0.18±0.01	23800
Inoculum*	7.21±0.49		6.53±0.41		

a. Sample on dry base
b. Sample on wet base
* All values are expressed in % except for the COD (mg/L)

2.2 VFA potential essays

In order to define the best operational conditions for VFA production from WAS, several tests will be assessed by means of acidogenic fermentation. Table 2. shows the experimental design carried out, in which was evaluated the initial organic load (OL) of the reactor (6 gVS/L and 4 gVS/L), the temperature (25 °C) and the initial pH (from 9, 10 and 11). Buffer solutions were used to manage the pH in the reactors. There were a total of 6 combinations tested by triplicate, the tests were carried out using batch reactors of 250 mL, amber bottles, with a working volume corresponding to the 80% of the total volume (Owen et al., 1979; Angelidaki et al., 2009). Substrate to inoculum ratio (S/X) was fixed as 1 in order to reduce the inhibitory effects during the fermentation. Reactors were filled with: inoculum; the fixed organic load, according with the initial characterization of the substrate; the buffer solution, depending on the combination; and the working volume was completed with distilled water. After this, the pH was adjusted with a NaOH solution. The reactors were hermetically sealed and placed in a thermostatic bath in order to guarantee the mesophilic condition set for a reaction time of 12 days in average. Finally, the biogas and VFA productivity was monitored by a destructive sampling. Every three days, the biogas composition was measured using BIOGAS 5000® Landtec and samples were collected for the further quantification of the VFA produced during the experiment time. Also, to follow up the biogas yield, a volume displacement system was set, using NaOH 0.5N solution as CO_2 trap (Cendales, 2011).

Table 2: Conditions of the experimental treatment for the acidogenic fermentation of WAS.

Condition of treatment	Organic Load (gVS/L)	Temperature (°C)	pH
C-1	6	25	9.5
C-2	6	25	10.5
C-3	6	25	11.5
C-4	4	25	9.5
C-5	4	25	10.5
C-6	4	25	11.5

2.3 Calculation for the VFA yield

he calculation of the VFA production efficiency, allows the assessment of the acidification potential of the WAS, where the specific yield is the ratio of total VFA concentration of the effluent, expressed on the VS equivalents per gram of VS fed, as shown in Eq (1) (Garcia-Aguirre et al., 2017).

$$VFA_{yield} = \frac{VFA_{out}}{VS_{in}} \quad (1)$$

2.4 Analytical methods

pH measurements were determined using a pH meter Edge model HI2002. Total solids (TS), volatile solids (VS) and organic matter (OM) content of the WAS and the effluent samples were determined by drying the samples at 105±5°C in an oven and the further calcination at 550±10°C in a muffle, this according to 2540B APHA - SM and D3174 of the America Society for Testing and Materials (ASTM). The Chemical Demand for Oxygen (COD) was measured using commercial Hanna Instruments vials with a range of 0 to 150 mg/L (HI 93752). Total Kjeldahl Nitrogen (TKN) was assessed according to the D1426 of the ASTM. Volatile fatty acids (VFA) and alkalinity (ALK) were measured according to standard methods (APHA, 2005). The measurement gas composition (CO_2, CH_4 and O_2%) was determined by the gas analyzer BIOGAS 5000® Landtec.

3. Results and Discussion

The VFA production was evaluated as a concentration of (mg COD/L), the production was measured every three days, in order to follow the behavior during the reaction time stablished. Figure 1 shows the time-course profile of the batch acidogenic fermentation of the WAS under the conditions established, where the higher total VFA production was achieved with an OL of 6gVS/L and a pH of 9.5 (1600 mg COD/L at day 12). Also, it can be observed that the fermentation started immediately; in most of the conditions tested, in most of the conditions tested, high productions of VFAs were registered during the first day of follow up. In accordance, in the essays with 4gVS/L, the C-6, achieved its highest production rate during day 3 (888 mg COD/L). In the anaerobic fermentation process, the high organic load is often used to improve acid production and shorten the fermentation period (Yuan et al., 2019); the results obtained shoes higher VFA production in the experiments with the higher initial organic load. Previous studies have found VFA production achievements around 540 to 1900 mg COD/L from the mixed culture fermentation of wastewater streams (Atasoy, et al., 2019).

In relation with the substrate to inoculum ratio, Iglesias-Iglesias et al., 2019 evaluated different S/X on the acidogenic fermentation of sewage sludge, registering concentration of VFA between 1800 and 2200 mg COD/L for a S/X of "1". The lower VFA concentrations obtained can be attributed to the higher concentration of total solids in the sewage sludge from El Salitre considering that existing research showed that substrate with high solid content could cause ammonium pressure, which could direct bacterial community structure toward enhanced syntrophic acetate oxidation reaction (Li et al., 2017b).

Figure 2 shows the VFA yields (g COD/g VS) of the WAS evaluated. The total VFA yield fluctuated from 0.08 to 0.27 for the conditions with 6 gVS and from 0.09 to 0.22 for conditions with 4gVS. Where the increase of the organic load seams to lead to a higher VFA accumulation and a decrease of pH favouring the fatty acid production (Iglesias-Iglesias et al., 2019; Zeng, Yuan, and Keller, 2006).

Concerning the general biogas composition registered in the experiments during the reaction time, there were measurements between 0.4-6.6% CH_4, 0.1-3.5% CO_2, 0.2-0.6% O_2, and 70-828 ppm of H_2S. In the case of C-4, after day 9, the experiment was interrupted due to the consumption of VFA by methanogens.

It is expected that pH tents to decrease until neutral conditions, generating a linear increase in the methane production, according to (Zhou et al., 2013). In this case by the 216 h (day 9) of fermentation, the cumulative production of methane would be around 250 mL of methane. Regarding VFA yield, the optimal pH value was 9.0; this value is consistent with previous researches (Huang et al., 2016).

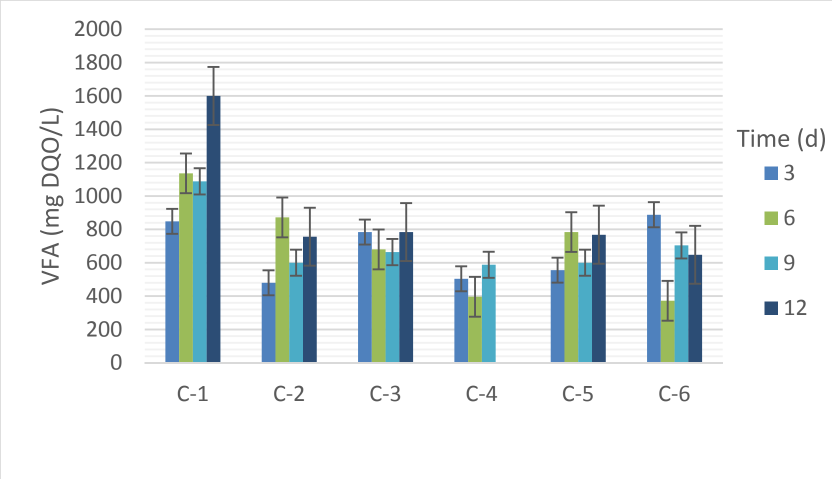


Figure 1: Acidogenic fermentation performance in terms of the VFA production during a reaction time of 12 days.

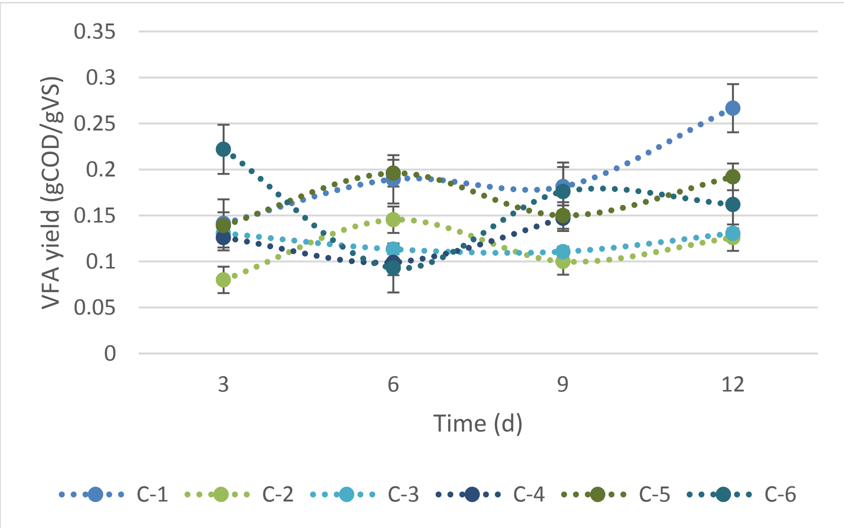
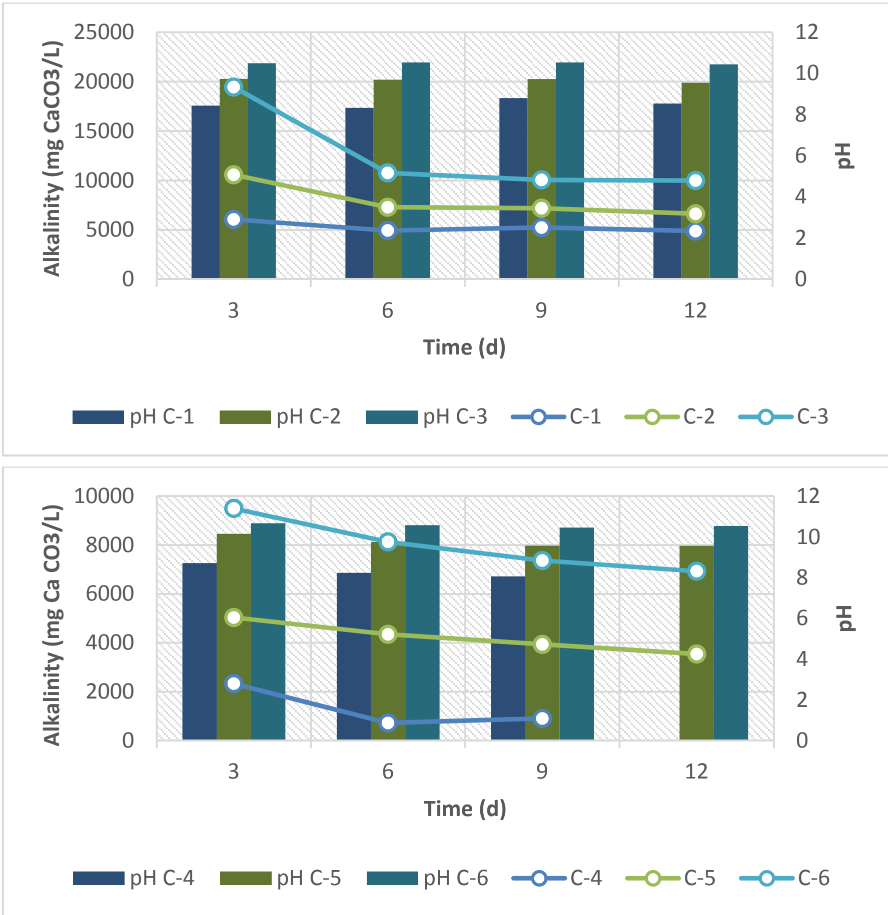


Figure 2: Acidogenic fermentation performance in terms of the VFA production efficiency during a reaction time of 12 days.

In anaerobic fermentation, pH is a critical process parameter that affects the productivity over the production of VFA, biohydrogen and methane production (Khan et al., 2016). The amount and quality of VFA produced is strongly attached to pH: pH values between 4.0 to 7.0, enhance the production of propionic and acetic acids; while pH values between 8.0 to 9.0 increases butyric acid production; according with previous researches, the optimal value for the production of VFA from wastewater streams is 10 (Kumar et al., 2019).
Figure 3 shows the alkalinity and pH variation, where values were reduced with the increase of the fermentation time, which can be related to the action of methanogens that transform the VFA into biogas and allow the process to be stable (Zhou et al., 2013; Huang et al., 2016). According with the results presented, some differences in terms of VFAs production were found for combinations with the same organic load and the levels of pH evaluated. Despite some previous works reported no relevant influence in VFA productions for similar ranges of pH, even though, alkaline conditions could result in a higher release of soluble carbohydrates and proteins. (Garcia-Aguirre et al., 2017; Iglesias-Iglesias et al., 2019).



(a)

(b)

Figure 3: Alkalinity and pH variation of the acidogenic fermentation performance, (a) for OL 6 gVS/L, (b) for OL 4 gVS/L.

4. Conclusions

Finally, the results obtained, can be consider an important highlight for the implementation of the most suitable acidogenic fermentation conditions for the further use of the VFA for the generation of PHAs due to the VFA concentrations obtained in the resulting experiments.
The highest yield was produced under an organic load of 6gVS/L and a pH of 9.5, where the methanogens were totally inhibited. However, it is necessary to continue experiencing different mixtures with sewage sludge, including primary sludge and at different temperatures, to determine which combinations are more favorable for the production of volatile fatty acids.
Alkalinity contributes to the production of VFA. VFAs production from alkaline fermentation of WAS is recommended as an alternative for the valorisation of waste streams from El Salitre WWTP.
With this research, it’s wanted to maximize the concentration of volatile fatty acids regardless of the type of VFA for now. Because, this would decrease operating costs in order to scale the process.

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