

# START-UP OF AN ANAEROBIC AVANCED REACTOR TREATING BIO-HYDROGEN EFFLUENTS USING A SEMI-SYNTHETIC FEED

Núñez F<sup>1</sup>, J.L. García-Morales J.L.<sup>1</sup>, Pérez M<sup>1</sup>

<sup>1</sup>Department of Environmental Technologies. Faculty of Marine and Environmental Sciences CASEM. University of Cádiz. Campus Río San Pedro s/n. E 11510 Puerto Real (Cádiz). Spain.  
E-mail: fabian.nunez@uca.es; joseluis.gacia@uca.es; montserrat.perez@uca.es

## Abstract

This study shows the start-up protocol of a methanogenic fixed-film reactor under thermophilic conditions (55°C) using biomass adapted to organic fraction of the municipal solid wastes (OFMSW) with FLOCOR-R as media support. Biohydrogen semi-synthetic substrate used was constituted by a mixed of the major products of the acidogenic anaerobic digestion processes: acetic, propionic and butyric acids in a ratio of 2:1:1, respectively, and the filtered effluent of an OFMSW methanogenic reactor. Laboratory reactor was fed in semi-continuous conditions. The anaerobic process was evaluated by quantification of different parameters in the feed and the effluent. At the end of the star-up process the volatile fatty acids removal efficiency was 95 % with a daily biogas production about 0.225 L CH<sub>4</sub>/L/d.

*Key words:* Volatile Fatty Acids (VFA) removal, anaerobic biofilm process, biohydrogen effluent.

## Introduction

One of the biological processes developed in the last years to utilize municipal solid wastes (OFMSW) for useful energy and materials recovery is the anaerobic digestion. High-rate anaerobic digesters which retain biomass have been popular in the waste treatment field because it has many advantages such as a high treatment efficiency and methane producing ability. Nowadays the generation of biohydrogen generation of this waste is also being considered as a viable alternative. This process generates environmentally clean energy (biohydrogen) and also stabilizes the waste. Thus, the biohydrogen fermentation technology could curtail the growing energy insecurity and eliminate the global and local pollution problems resulting from excessive use of fossil fuels. The biohydrogen fermentation technology could enhance the economic viability of many processes utilizing hydrogen as a fuel source or as a raw material (Sung et al., 2003).

When a high COD waste, such as OFMSW, is treated in a two-phase anaerobic system, volatile fatty acids (VFA) –mainly acetic, propionic and butyric acids – are produced in the biohydrogen effluent into the acidification reactor and converted to CH<sub>4</sub> and CO<sub>2</sub> in the following methanogenic reactor.

This study evaluates the start-up protocol of an anaerobic fixed-film reactor under thermophilic conditions (55°C), with a plastic media support (FLOCOR-R), using a new substrate. Sometimes, it is necessary to use synthetic substrates to proceed the start-up of a reactor. In this case, initially, there was no real acidogenic substrate, so a semi-synthetic feed was used.

## Methods

**Laboratory reactor:** The start-up process of support media was carried out in an anaerobic fixed-film reactor. The laboratory reactor consisted on a vertical cylindrical tank (length 25 cm, internal diameter, 10 cm), with a total volume of 2.5 L and active volume of 2.25 L (volume of FLOCOR-R plastic support). The reactor temperature was maintained at  $55 \pm 1^\circ\text{C}$  by circulating water through the water jacket and the biogas generated was collected in a gas meter. Effluent recirculation was used to mix and homogenise the liquid in the system. Recirculation Ratio (R) is defined as the ratio of recirculation flow and active reactor volume. This parameter has units of  $\text{d}^{-1}$  and represents the number of times daily that circulates a volume equivalent to active reactor volume. FLOCOR-R was chosen because of its characteristics: Corrugated plastic tubes of 16 mm in diameter (non-porous media) of low density ( $1.161 \text{ kg L}^{-1}$ ), high porosity (93.71 %), and high specific surface ( $450 \text{ m}^2 \text{ m}^{-3}$ ) suitable for using stationary packed media in filter reactors.

**Inoculum:** The inoculum was obtained from a stirred tank reactor of a pilot plant working in thermophilic anaerobic digestion of the OFMSW that operated in optimal conditions at the time of sampling. The pilot plant was located in an industrial plant for recycling municipal solid waste (Municipal Wastes Treatment Plant "Las Calandrias", which is located in Jerez de la Frontera, Spain).

**Substrate:** The substrate used was the effluent of a methanogenic digester treating OFMSW from the same facility. In the first step, the effluent with high solids contents was separated as solid and liquid effluent by using filter bags (Teknofanghi®). The major intermediate products of acidogenic anaerobic digestion such as acetic, propionic and butyric acids were mixed and added in the liquid effluent in a ratio of 2:1:1, respectively (This ratio was suggested by several authors to simulate acidogenic effluents: Speece and McCarty, 1964; L. CHiu-Yue, 1985), and used to simulate a biohydrogen semi-synthetic substrate for feeding into reactor. It was used to the production of biogas in a second step of the methanogenic anaerobic digestion and the solid effluent would be subjected to composting. The main composition of the semi-synthetic feed is shown on Table 1.

**Analyses:** Chemical Oxygen Demand (COD), volatile suspended solids (VSS) and pH were determined by Standard Methods (APHA, AWWA, WPCF, 1989). Both the Volatile Fatty Acids (VFA, total and individual compounds) and biogas composition ( $\text{CH}_4$  and  $\text{CO}_2$ ) were analysed by gas chromatography (García-Morales et al., 1997).

**Table 1.** Main characteristics of the semi-synthetic feed

| <b>Parameters</b>     | <b>Concentration</b> |
|-----------------------|----------------------|
| acetic acid (mg/L)    | 7131.06              |
| propionic acid (mg/L) | 4318.07              |
| n-butyric acid (mg/L) | 4564.6               |
| pH                    | 5.74                 |
| COD (mg/L)            | 40250                |
| VSS (mg/L)            | 3059.17              |

## Results and discussion

For the start-up process, initially the inoculum was added to the support (FLOCOR-R) without recirculation in order to begin the initial pre-coating process of bacterial colonization (García-Morales et al., 1997). After 2 weeks, the reactor was fed with the semi-synthetic feed, with an initial HRT of 25 days and with a low rate of recirculation ( $R: 89.51 \text{ d}^{-1}$ ) to facilitate the growth of the attached biomass and biofilm development. When an increase in the removal of VFA was shown, the agitation by recirculation was increased ( $R: 188.23 \text{ d}^{-1}$ ), in order to promote homogeneity of the media and facilitate the transfer between the substrate and the attached microorganisms (Figure 1).

The biogas production and removal rate of VFAs in the reactor were studied. The reactor was operated until a steady-state performance was reached, as marked by consistent gas production, an effluent VFA concentration and the constancy of pH around 8.

The main experimental results are represented in the following figures:

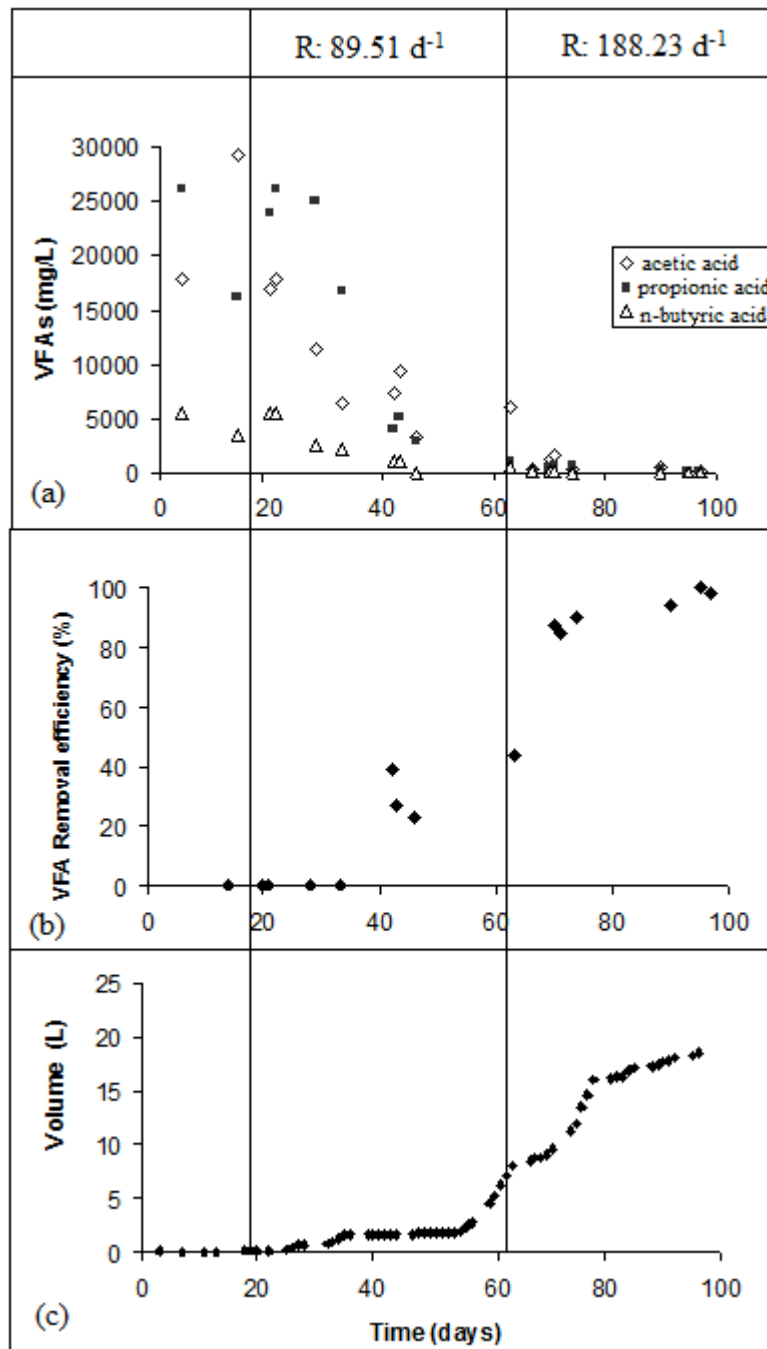


Figure 1: Variation of the characteristic parameters of the anaerobic process: (a) Temporal evolution of VFA concentration (mg/L) in the star-up period; (b) Temporal evolution of VFA Removal efficiency (%); (c) Evolution of volume of methane accumulated (L).

Figure 1-a shows the temporal evolution of the VFA. The VFA are initially present in the reactor at concentrations above 25000 mg AcOH/L, until day 40 in which begin to decrease. This reduction coincides with a significant increase in biogas generation as shown Figure 1-c with a stable composition (80% CH<sub>4</sub> and 20% CO<sub>2</sub>), and also a stabilized concentration of VSS in the effluent (780 mg/L).

From day 60 the results shows that an increase in the ratio of recirculation causes a good homogenization of the medium, with a better transfer of substrate to the biofilm, and therefore increased VFA removal efficiency (Figure 1-b).

After this period, HRT was decreased to 10 days and the reactor was fed with a real biohydrogen effluent. Thus, high removal efficiencies were shown, which is indicative of bacterial population obtained on the start-up process is adequate to degrade these effluents.

## Conclusions

A fixed-bed technology non-porous plastic support FLOCOR-R type is suitable for waste treatment readily. The physico-chemical presents FLOCOR-R make it highly suitable for operation in fixed bed as the high porosity of the bed prevents any clogging phenomena associated with this technology.

The support characteristics and the described colonisation protocol allow to start-up the biofilm reactor in a short length of time, with a rapid biofilm development and reduced the lag periods.

The experimental results obtained indicate that anaerobic filters can remove high concentrations of VFAs. The volatile fatty acids removal efficiency was 95 % with a daily biogas production about 0.225 L CH<sub>4</sub>/L/d. Methanogenic reactor start-up using a semi-synthetic acidogenic effluent was carried out successfully.

## Acknowledgements

This work and Fabian Nuñez contract was supported with Ministry of Science and Innovation (MICINN), Spain. Project CTM2007-62164/TECNO. The authors thank the Municipal Waste Treatment Plant "*Las Calandrias*" its collaboration in the project.

## References

- APHA, AWWA, WPCF (1989) Standard Methods for the Examination of Wastewater. Ed. Rhodes Trussell. 17<sup>th</sup> edn. APHA. Washington, DC.
- Lin, C; Sato, K; Noike, T; Matsumoto, J; (1985). Methanogenic digestion using mixed substrate of acetic, propionic and butyric acids. *War. Res.* Vol. 20, No. 3, pp. 385-394.
- Sans, C; Mata-Alvarez, J. (1994). Volatile fatty acids production by anaerobic fermentation of urban organic wastes.
- Michaud, S ; Bernet, N ; Buffière, P ; Roustan, M ; Moletta, R. (2001). Methane yield as a monitoring parameter for the start-up of anaerobic fixed film reactors. *Water Research* 36 (2002) 1385-1391.
- Pérez, M; García-Morales, J.L; Romero, L.I; Sales, D. (2006). Anaerobic thermophilic colonization of porous support. *Chem. Biochem. Eng. Q.* 20 (2) 203-208.
- Pérez, M; Romero, L.I; Nebot, E; Sales, D. (1996). Colonisation of a porous sintered-glass support in anaerobic thermophilic bioreactors. *Bioresource Technology* 59 (1997) 177-183.

- Sung, S; Bazylinski, D; Raskin, L; (2003). Biohydrogen Production from Renewable Organic Wastes. Hydrogen, Fuel Cells, and Infrastructure Technologies FY 2003 Progress Report
- Yu, J; Pinder, K.L. (1993). Utilization of volatile fatty acids in methanogenic biofilms. Bioresource Technology 46 (1993) 241-250.