

Acidogenic fermentation and anaerobic co-digestion of mechanically sorted OFMSW and Polyethylene glycol

J. Dosta¹, A. Martin-Ryals², M. Garrigó¹, V. Ortiz-Roca¹, I. Fernández¹, J. Mata-Álvarez¹

¹Department of Chemical Engineering and Analytical Chemistry, University of Barcelona, Barcelona, Catalunya, 08080 Spain.

²Department of Agricultural and Biological Engineering, University of Illinois Urbana-Champaign, Urbana, IL, 61801, USA

Presenting author email: jdosta@ub.edu

Abstract:

This study is focused on the anaerobic biological treatment of a PEG-rich industrial wastewater and mechanically sorted OFMSW, called Residual Organic Matter (ROM), in order to assess the effects of mixing these substrates to produce VFA through anaerobic co-fermentation or biogas through anaerobic co-digestion. As a consequence of the anaerobic co-digestion of PEG and ROM (PEG representing a 3.5% v/v), the Specific Methane Production (SMP) reached 0.44 m³ CH₄ (kg VS day)⁻¹ in front of 0.30 m³ CH₄ (kg VS day)⁻¹ of the AD control reactor, with just a 35% higher OLR on VS basis. The fast degradation of PEG implied that effluent quality was nearly the same of AD process, showing high stability with neither increase of VS nor significant variations in nutrients and heavy metals content. Acidogenic fermentation was carried out in batch tests for several mixtures of PEG industrial wastewater and ROM, where the percentages of PEG-rich wastewater on VS basis were 0, 12.5, 25, 37.5 and 50%. The best results of VFA increase per unit of VS of co-substrate fed was obtained for the mixture with 12.5% of PEG wastewater at 5 days retention time. The same mixture was fed in an anaerobic fermenter under mesophilic conditions treating ROM at an HRT of 3.5 days and without modifying the OLR (VS basis). As a consequence of this co-fermentation, the production of VFA was increased by 14% (12.1 g VFA L⁻¹) when compared with the values obtained in mono-fermentation. Moreover, the percentage of acetic acid + propionic acid (66.5 %) was in the range than that obtained with mono-fermentation of ROM (64.6 %).

Keywords: Anaerobic co-digestion, Acidogenic fermentation, Biogas, OFMSW, PEG, VFA

1- INTRODUCTION

Polyethylene glycol (PEG) has many applications, from industrial manufacturing to medicine production, and it can be found in some industrial wastewaters. Some studies have showed that PEG can be anaerobically metabolized in order to recover energy in the form of biogas (Kawai, 2002). Anaerobic biological treatment of pure PEG could be limited by the lack of nutrients and low alkalinity, so it could be digested with other substrates, such as Organic Fraction of Municipal Solid Waste (OFMSW), in order to create a synergistic effect to overcome these limitations.

The anaerobic co-digestion (AcoD) of OFMSW (all qualities) as a main substrate has not been as studied as manures or sewage sludge (Mata-Álvarez *et al.*, 2014). Most of the studies have been focused in the anaerobic co-digestion of this biowaste (with high biogas potential) with sewage sludge (main substrate) in existing municipal WasteWater Treatment Plants (WWTP) because these digesters are usually characterized by an extra capacity around 30% (Montusiewicz *et al.*, 2011, Krupp *et al.*, 2005). However, for existing mechanical-biological treatment plants of OFMSW where anaerobic digestion is used, the use of a co-substrate as

PEG could enhance biogas production since its characteristics are complementary to those of OFMSW.

On the other hand, in recent years the acidogenic fermentation of biodegradable organic wastes (for example, OFMSW and PEG), has gained more attention to produce valuable products such as Volatile Fatty Acids (VFA), which are feedstock for the production of value-added chemicals (Pavan *et al.*, 2014). The acidogenic fermentation of OFMSW using mixed cultures is an effective process to produce VFA (Bolzonella *et al.*, 2005). Key operating parameters, such as the Hydraulic Retention Time (HRT), Solid Retention Time (SRT), pH, temperature and the Organic Loading Rate (OLR), among others, should be tuned in order to promote VFA generation and to adjust the desired VFA composition, depending on its downstream applications (Lee *et al.*, 2014).

This study is focused on the anaerobic biological treatment of a PEG-rich industrial wastewater and mechanically sorted OFMSW, in order to assess the effects of mixing these substrates to produce biogas through anaerobic co-digestion or VFA through anaerobic co-fermentation.

2- MATERIALS AND METHODS

2.1. Experimental set-up

For the anaerobic co-digestion of mechanically sorted OFMSW, called Residual Organic Matter (ROM), and PEG-rich industrial wastewater, two lab-scale jacketed and watertight anaerobic digesters of 4 L of effective capacity (A and B) were run under mesophilic conditions (35 ± 0.1 °C). The reactors were equipped with mechanical stirrers (*Heidolph*, RZR 2020) and a biogas counter (*Ritter*, MGC-1 V.3.1). A fraction of the produced biogas was collected in a flask to analyse its composition. The operations of feeding and withdrawal were performed manually once a day. Initially, the reactors were fed with ROM and after a period of more than 3 times the retention time, one of these digesters (reactor B) was fed with a mixture of ROM and PEG-rich industrial wastewater, in order to assess the improvement of biogas production and the stability of the anaerobic co-digestion process.

For the acidogenic fermentation of these substrates, the effect at short time of treating several ROM/PEG mixtures was studied in anaerobic batch tests (250 mL) under mesophilic conditions, where VFA production and VS content was followed over 7 days of operation. Afterwards, a lab-scale anaerobic fermenter (5L of effective capacity; temperature controlled at 37 ± 0.1 °C, mechanically stirred) was operated in order to analyse the long-term effect of using the ROM/PEG mixture that yielded the best results at short-term conditions. The feeding and withdrawal of the fermenters were performed manually once a day, introducing nitrogen gas during this process to prevent the entrance of air into the reactors.

2.2. Substrate and inoculum

The ROM was collected in an industrial mechanical-biological treatment plant of the Barcelona Metropolitan Area (Spain) and the PEG-rich industrial wastewater came from a pharmaceutical industry (see its characteristics in Table 1).

The anaerobic digesters and the fermenter were inoculated with anaerobically digested sludge from the full-scale AD plant treating the ROM used in this work. After collection, all samples were stored at 4 °C until its utilization.

Table 1 - PEG-rich industrial wastewater characterization

Parameter	Units	Value
pH	-	4.5-5.0
Total Solids (TS)	% w/w	45.04 ± 1.02
Volatile Solids (VS)	% w/w	44.61 ± 1.03
Total Alkalinity	mg CaCO ₃ L ⁻¹	1,867.5 ± 42.5
Total VFA	mg L ⁻¹	657.4 ± 1.5
NH ₄ ⁺ -N	mg L ⁻¹	5.15 ± 0.5
NO _x ⁻ -N	mg L ⁻¹	n.d.
Sulfites and sulfates (SO _x ²⁻ -S)	mg L ⁻¹	n.d.

n.d.: not detected

2.3. Analytical methods

Total solids (TS), volatile solids (VS), COD and NH₄⁺-N were determined according to the standard methods 2540G (APHA, 2012). Total (TA) and partial (PA) alkalinity were determined by a titration method at pH 4.3 and 5.75, respectively, and the intermediate alkalinity (IA) by the difference between TA and PA. Individual VFA were analysed by a HP 5890-Serie II chromatograph equipped with a capillary column and flame ionization detector. The biogas composition was determined with a Shimadzu GC-2010+ gas chromatograph equipped with a thermal conductivity detector and a Carboxen[®] column. The biogas and methane productions are reported at standard temperature and pressure conditions (i.e. 0 °C and 1 bar).

3. RESULTS AND DISCUSSION

3.1. Anaerobic co-digestion of ROM and PEG-rich industrial wastewater.

Figure 1 shows the Organic Loading Rate (OLR) applied and the results of specific methane production (SMP) for the periods of ROM mono-digestion and co-digestion with PEG-rich wastewater in reactors A and B, respectively. On the first stage, where anaerobic mono-digestion of ROM at an HRT of 20 days was carried out, the methane production was similar between both reactors, with an average SMP of 0.31 and 0.29 m³ CH₄ (kg VS day)⁻¹, for reactor A and B, respectively. In this period, the ROM fed to the digesters contained an average of 5.02 ± 1.07 % TS and 3.88 ± 0.89 % VS. The percentage of TS and VS removal were, respectively, 60.27 ± 3.37 % and 73.84 ± 1.48 % for reactor A and 63.88 ± 1.03 % and 77.45 ± 1.83 % for reactor B, so the performance of both digesters was very similar. Regarding the biogas composition, during this stage the methane percentage in the produced biogas was nearly 60% in volume (namely, 61.4 ± 0.72 % CH₄ for Reactor A and 59.9 ± 0.74 % CH₄ for Reactor B). VFA concentration in the digesters were always below 230 mg L⁻¹ and were mainly composed by acetic acid. During the last two weeks of the mono-digestion stage, the average total VFA concentration was 143 ± 24 mg/L for Reactor A and 141 ± 29 mg/L for Reactor B and, therefore, the acid alkalinity was low. For both digesters, pH remained in the range of 7.7 ± 0.1 in this whole period.

On the second stage, co-digestion of ROM and PEG was implemented in reactor B. PEG was progressively increased until it reached a 3.5% v/v in the mixture of ROM/PEG. During the co-digestion period (HRT 20 days; PEG 3.5% v/v), the total OLR applied (average value 2.25 kg SV (m³ reactor day)⁻¹) suffered high variations due to changes in the composition of the ROM. Therefore, the OLR related to PEG was nearly constant (0.78 kg SV (m³ reactor day)⁻¹) while the OLR due to the ROM was 1.47 ± 0.43 kg SV (m³ reactor day)⁻¹. As a consequence of AcoD implementation in digester B, SMP clearly increased in the co-digestion process reaching 0.44

$\pm 0.08 \text{ m}^3 \text{ CH}_4 \text{ (kg VS day)}^{-1}$, in front of $0.29 \pm 0.02 \text{ m}^3 \text{ CH}_4 \text{ (kg VS day)}^{-1}$ of the AD control reactor, which represents an increase of approximately 50% in relative production. The percentage of CH_4 in the produced biogas of both reactors did not present significant differences. At the same time, reactor B showed stability throughout the AcoD implementation. The VFA generation did not influence the pH stability due to high system alkalinity (over $5 \text{ g CaCO}_3 \text{ L}^{-1}$) and the nutrients content of the ROM compensated its deficit on the PEG-rich wastewater. The fast degradation of the PEG implied that effluent quality was nearly the same of AD process, with neither increase of VS nor significant variations in nutrients and heavy metals content. The VFA concentration in the effluent of the co-digestion reactor was $195 \pm 30 \text{ mg L}^{-1}$. Moreover, the $\text{NH}_4^+\text{-N}$ concentration in the co-digestion effluent was slightly lower than that obtained in the reference reactor (mono-digestion of ROM). However these values were very dependent on the ROM samples fed; in the last two weeks of experimentation, $\text{NH}_4^+\text{-N}$ in reactor B (co-digestion) and reactor A (mono-digestion) were $1.94 \pm 0.08 \text{ g NH}_4^+\text{-N L}^{-1}$ and $2.07 \pm 0.09 \text{ g NH}_4^+\text{-N L}^{-1}$, respectively.

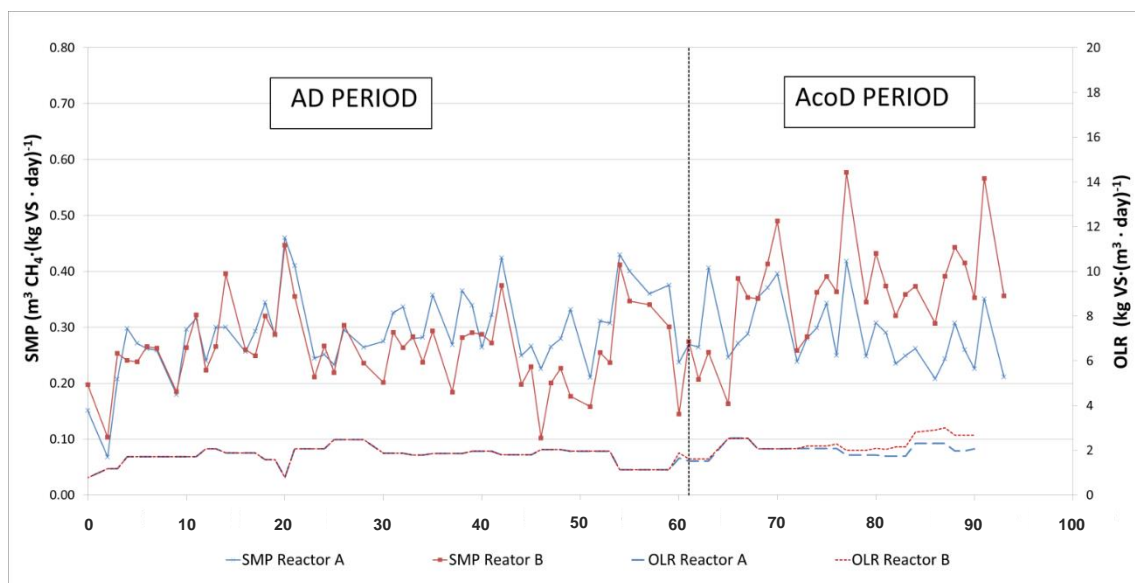


Figure 1 – Specific Methane Production (SMP) and Organic Loading Rate (OLR) along the study on anaerobic digestion reactors A and B

3.2. Fermentation of ROM and co-fermentation of ROM and PEG-rich industrial wastewater.

As a previous step to ROM fermentation, several batch tests were carried out to assess proper operational conditions at short term in order to maximize VFA production from this biowaste. The influence of three operational parameters was studied: solids concentration (from 3.3 to 6.1% TS), temperature (33-37°C) and retention time (batch tests duration was set at 5 days). Batch fermentation tests were performed and analysed using surface response curve methodology to determine optimal operating parameters. Higher VFA production was registered at the highest temperature tested, namely 37°C. Figure 2 shows the response curve resulting from batch fermentation of ROM at 37°C. When comparing the resulting VFA concentrations at various retention times and solids concentrations, it was concluded that maximum VFA production under short-term conditions was achieved at 5.4% TS and 3.4 days of retention time, under 37°C.

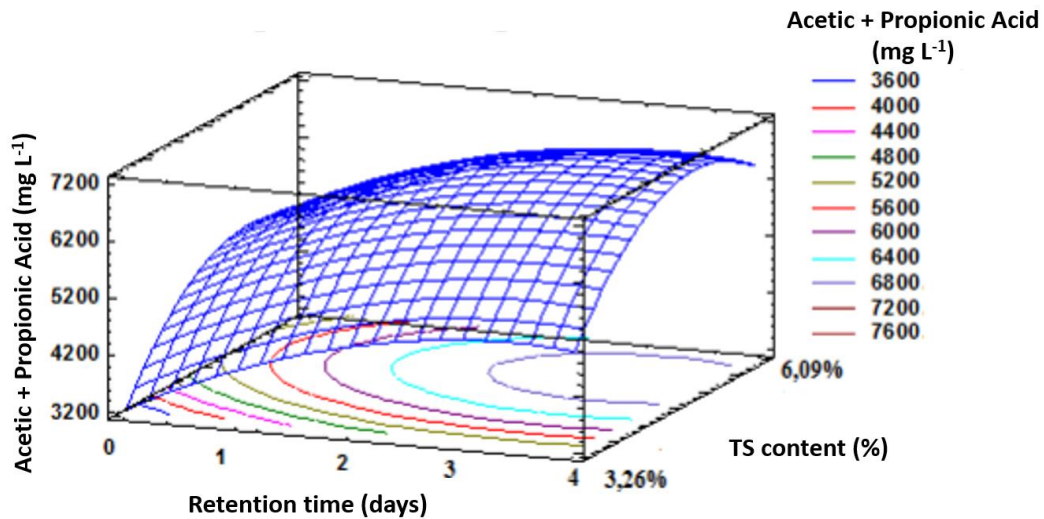


Figure 2. Surface response curve from batch test fermentation of ROM at 37°C comparing resulting VFA concentrations at various retention times and solids concentrations.

Considering the optimal short-term operational parameters, a lab-scale continuous fermentation reactor (working temperature 37°C) was set-up and investigated to assess the production of VFA under long-term conditions. Figure 3 shows VFA production in the continuous fermenter over a range of HRTs from 2.5 to 3.5 days, where the average TS concentration of the influent ROM was in the range of $45.7 \pm 10.2 \text{ g L}^{-1}$. In Figure 3, it can be observed that VFA concentrations increased with increasing HRT, although it was also dependent on the feed substrate (see initial VFA concentration). Average VFA concentrations at 2.5, 3.0, and 3.5 days HRT were $8,880 \pm 765$; $9,359 \pm 1,506$; $11,886 \pm 1,360 \text{ mg L}^{-1}$, respectively. Moreover, longer retention time resulted in a greater proportion of acetic and propionic acid within the total mixture of VFAs produced. Acetic acid represented an average percentage of 35.2, 37.5 and 45.3% of the total VFA generated in the fermentation reactor for HRT 2.5, 3.0 and 3.5 days, respectively. However, it should be highlighted that the ROM fed in the last period (HRT 3.5 days) contained more VFA than that used in the previous periods.

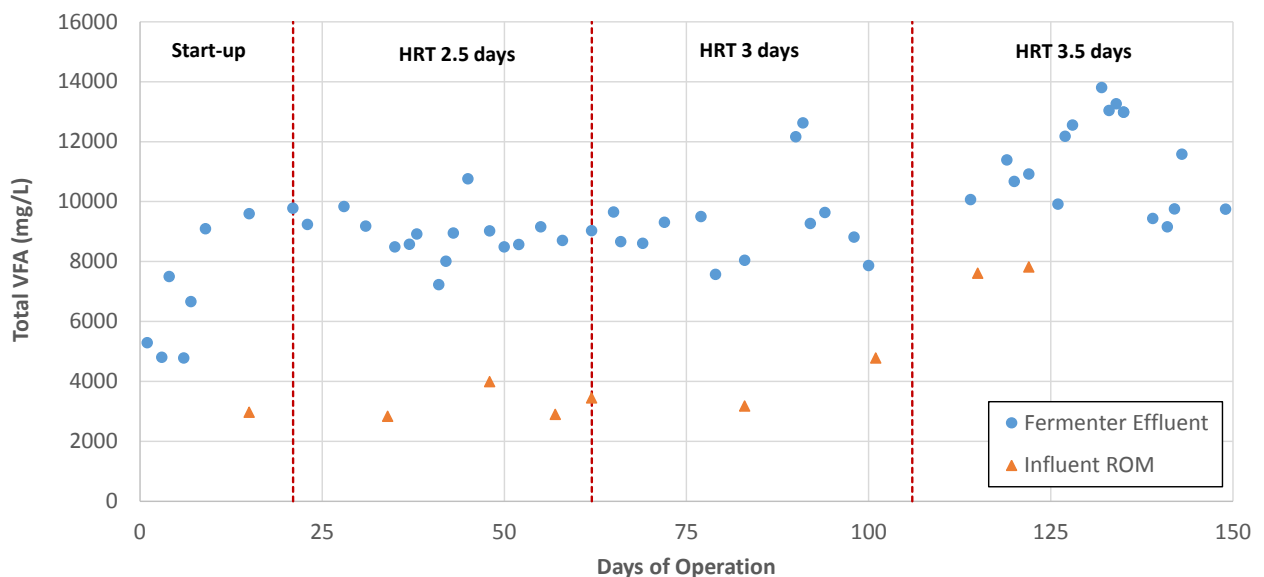


Figure 3. Concentration of total VFA (influent and effluent) in the lab-scale continuous fermenter over time.

Anaerobic batch tests for evaluating the effect of mixing ROM and PEG-rich industrial wastewater on the acidogenic fermentation performance were carried out, where the percentage of PEG-rich wastewater on VS basis was 0, 12.5, 25, 37.5 and 50%. The highest VFA increase per unit of VS of PEG added was obtained in the test of 12.5% PEG wastewater at 5 days retention time, which accounted for a 34% higher total VFA produced with respect to that obtained with mono-fermentation. However, higher PEG content resulted in a higher proportion of VFA of 4C or more, as stated in Figure 4, where the composition of VFA obtained in the acidogenic fermentation batch tests are shown.

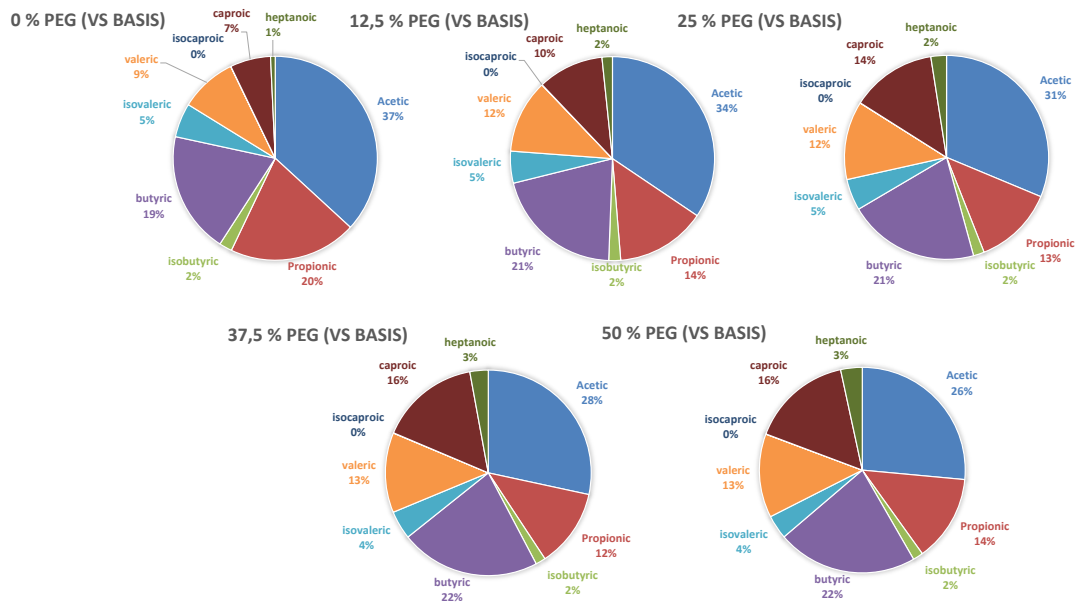


Figure 4 - Composition of VFA obtained in the acidogenic fermentation batch tests of ROM and PEG-rich industrial wastewater.

In order to assess the long-term effect of adding 12.5% on VS basis on the acidogenic fermentation, a lab scale digester was operated at HRT 3.5 days and 37°C during 33 days with real ROM. During the first period of mono-fermentation, TS concentration was 5.01 ± 1.14 %, yielding slightly lower VFA concentrations ($10,667 \pm 1,676$ mg L⁻¹) than that obtained in the experiments presented in Figure 3 (the ROM was collected in a different period). However, the percentage of acetic acid (48.5 ± 5.9 %) was similar than that obtained in the previous run of the fermenter. After this period, a mixture of ROM and PEG-rich industrial wastewater (this co-substrate represented the 12.5% of VS) was co-fermented maintaining the same HRT and operating temperature (3.5 days, 37°C) during 15 days of operation (the process is still running) and maintaining the OLR on VS basis from the previous period. In this co-fermentation stage, the production of VFA was increased by 14% ($12,120 \pm 1,275$ mg L⁻¹) when compared with the values obtained in mono-fermentation, which is in good agreement with the results obtained in the batch tests (note that the VS related to ROM fed to the digester were 12.5% lower than in the previous stage). Moreover, the percentage of acetic acid + propionic acid (66.5 ± 3.5 %) was in the range than that obtained in the previous stage (64.6 ± 4.6 %), and were above than those values expected considering the batch tests. This fact suggests an acclimation of the mixed culture present in the fermenter to treat this biowaste and it is also consistent with that obtained in the anaerobic co-digestion of PEG and ROM, where the low concentration of VFA in the effluent were mainly composed by acetic acid.

Considering the aforementioned results, PEG-rich industrial wastewaters could be co-treated with mechanically sorted OFMSW for both increasing the VFA generation in an acidogenic fermentation process and/or for enhancing biogas production in anaerobic digestion without affecting considerably the anaerobic digestion process stability and the digestate quality. A pilot scale experimentation would be advisable before scaling up to confirm these results and that no other problems appear.

4 - CONCLUSIONS:

The impact of mixing mechanically sorted Organic Fraction of Municipal Solid Waste (OFMSW) or Residual Organic Matter (ROM) and a Polyethylene Glycol (PEG) rich industrial wastewater in acidogenic fermentation tests and anaerobic digesters has been assessed in this study yielding promising results for both systems.

The use of PEG-rich industrial wastewater as co-substrate has been assessed as a feasible alternative to improve biogas production in the anaerobic digestion of ROM, without affecting the reactor stability and with no external nutrient supply. When the OLR was increased by 35% (on VS basis) due to co-substrate addition, an increase of the SMP by approximately 50% was registered without affecting the digestate quality

Regarding the acidogenic fermentation of ROM, the introduction of PEG-rich industrial wastewater (co-substrate) lead to higher VFA production. The highest VFA increase per unit of VS of PEG wastewater added was recorded for a mixture of ROM and PEG with 12.5 % of co-substrate on VS basis. In short-term assays (anaerobic batch tests) the proportion of VFA of C4, C5 and C6 was higher when compared with acidogenic fermentation of ROM. However, during long-term experiments of co-fermentation (12.5 % on VS basis of PG co-substrate) an acclimation of biomass was observed and higher percentages of acetic acid and propionic acid (66.5%) to total VFA were recorded, with an increase of VFA production of 14% with respect to mono-fermentation of ROM (maintaining the OLR on VS basis).

ACKNOWLEDGEMENTS

The authors are grateful to the Spanish Ministerio de Economía y Competitividad for its financial support (CTM2016-76275-R and RedNovedar CTQ2014-51693-REDC projects). Ana Martín-Ryals would also like to acknowledge the U.S. Fulbright Program for providing a Graduate Research Fellowship to conduct this research.

REFERENCES

- APHA, AWWA, WEF (2012) Standard Methods for the Examination of Water and Wastewater, 22nd ed., Washington DC.
- Bolzonella, D., Fatone, F., Pavan, P, Cecchi, F. (2005) Anaerobic fermentation of organic municipal solid wastes for the production of soluble organic compounds. *Industrial & Engineering Chemistry Research*, 44, pp. 3412-3418.
- Kawai, F. (2002) Microbial degradation of polyethers. *Applied Microbiology and Biotechnology*, 58(1): p. 30-38.
- Krupp, M., Schubert, J., Widmann, R. (2005) Feasibility study for co-digestion of sewage sludge with OFMSW on two wastewater treatment plants in Germany. *Waste Management*, 25, pp. 393–399.
- Lee, W.S., Chua, A.S.M., Yeoh, H.K., Ngoh, G.C. (2014) A review of the production and applications of waste-derived volatile fatty acids. *Chemical Engineering Journal*, 235, pp. 83–99

- Mata-Álvarez, J., Dosta, J., Romero-Guiza, M., Fonoll, X., Peces, M., Astals, S. (2014) A critical review on –Anaerobic Co-digestion achievements between 2010 and 2013. *Renewable & Sustainable Energy Review*, 36; 412–427.
- Montusiewicz, A., Lebiocka, M. (2011) Co-digestion of intermediate landfill leachate and sewage sludge as a method of leachate utilization. *Bioresource Technology*, 102, pp. 2563–2571.
- Pavan, P. (2014). Tendencias y oportunidades para la gestión de la fracción orgánica de los residuos municipales. *Actas de las XI Jornadas sobre biometanización de RSU. Biometa'2014*. Barcelona.