CHEMICAL ENGINEERING TRANSACTIONS

VOL. 86, 2021

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš

ISBN 978-88-95608-84-6; **ISSN** 2283-9216

Development of a biorefinery platform for urban waste valorisation into biogas and added-value products

F. Valentino[b], L. Lorini[a], P. Pavan[b], M. Majone[a]

[a] Department of Chemistry, “La Sapienza” University of Rome, P.le Aldo Moro 5, 00185 Rome, IT
[b] Department of Environmental Science, Informatics and Statistics, Via Torino 155, 30170 Venezia Mestre, IT
francesco.valentino@unive.it

This study focuses on the application of the circular economy approach, with generation of energy and production of added-value products from organic waste, while minimizing environmental impacts. Within this purpose, an urban biorefinery technology chain has been designed at pilot scale for the production of biogas and biopolymers (polyhydroxyalkanoates, PHA). The pilot system (100-400 L) comprised different units: a) biowaste acidogenic fermentation; b) solid/liquid separation unit (a coaxial centrifuge and a tubular ultrafiltration membrane); c) a Sequencing Batch Reactor (SBR) for the production of aerobic PHA-storing biomass; d) aerobic fed-batch PHA accumulation reactor and e) anaerobic co-digestion (ACoD). The thermal pre-treatment of the biowaste before mesophilic fermentation increased the carbon conversion into volatile fatty acids (VFA), being the final VFA/COD_{SOL} (soluble COD) higher than 0.80. The VFA-rich stream was utilized in a high-rate SBR for the enrichment of PHA-accumulating biomass, at short solid retention time (SRT of 1 d), 12 h of cycle length and 4.0 gCOD/L d as organic loading rate (OLR). The aerobic biomass was characterized by a high accumulating capacity (with PHA content around 60% on cell dry weight). The global PHA yield of 0.1 kg PHA/kg VS (volatile solids) was estimated as the best scenario. The excess sludge and the solid-rich biorefinery overflows were utilized for biogas production in a dedicated anaerobic digestion section to sustain a closed loop approach and to prevent secondary wastes production.

1. Introduction

Recent strategies in the European Union (EU) set, as a priority, the transition towards a circular economy by adopting the “closing the loop” approach to industrial production systems (Maina et al. 2017). One of the objectives of this strategy is to maintain the value of products, materials and resources in the economy for the longest time possible, together with the objective of waste minimization (European Commission 2015). The conversion of low value products into higher value products, consistent with the EU approach to the circular economy, can be realized with the application of a biorefinery technology chain. The biorefinery represents a way to conduct the valorisation of the renewable resources, providing high value marketable products and minimizing both energy consumption and waste generation (Andersen et al. 2018). The use of renewable resources such as biomass or even organic waste can be challenging due to the competition with economically inexpensive fossil fuel energy. End-product identification and cost-effecting processing schemes are key elements in the biorefinery design, allowing the development of competitive technologies (Zabaniotou et al. 2019). The creation of a biorefinery using organic waste as starting substrate can contribute to both waste disposal problems and renewable resources valorization. In urban contexts, two of the most available organic substrates are food waste and wastewater sludge. Food waste production in Europe accounts for about 87.6 million tons annually (Colombo et al. 2017). Two of the most common processes applied for sewage sludge disposal are composting or anaerobic digestion. Anaerobic digestion of one or more organic substrates is a process currently applied also in the sludge line of existing wastewater treatment plants (WWTPs), in order to stabilize organic matter along with the production of biogas (Mata-Alvarez et al. 2014). The application of a biorefinery technology chain in urban scenarios, where organic substrates are always available, can foster the combination and valorization of different substrates into added-value marketable products other than biogas alone (Estevez-Alonso et al. 2021). In the present study, an urban biorefinery technology chain was developed at pilot scale inside the Treviso WWTP (northern Italy). The Treviso province showed optimum conditions for the application of such technology, since waste separated collection is very efficient. Organic fraction of municipal solid waste (OFMSW) and sewage sludge from the municipal WWTP were combined together for biogas and polyhydroxyalkanoates (PHA) production by mixed microbial cultures (MMCs). The performances of each single unit were analysed and the whole technology chain was assessed with a full mass and energy balance.

2. Materials and Methods

A mixture of OFMSW and sewage sludge was fed to the acidogenic fermenter in 30% and 70% volumetric ratio, respectively. The fermented stream, enriched in volatile fatty acids (VFAs), was sent to the solid-liquid separation unit for further refining (suspended solids removal) before being fed to the following aerobic steps: the SBR and fed-batch reactor for biomass selection and PHA accumulation, respectively. The overflows, namely the solid-rich fraction from the solid-liquid separation unit, were sent to anaerobic co-digestion reactor together with excess sewage sludge produced in the contiguous full-scale plant for municipal wastewater treatment. Activated sludge from the full-scale plant was used as inoculum for the SBR and the biomass was selected under an aerobic dynamic feeding, formally known as feast-famine regime (Valentino et al., 2017). The surplus PHA-producing biomass was then utilised for the PHA accumulation within the microbial cells..

2.1 Anaerobic steps: fermentation and co-digestion

The anaerobic line consisted of the fermentation and digestion reactors. The anaerobic fermentation was carried out in batch mode in a 380 L reactor equipped with a mechanical stirrer, under the following operating conditions: hydraulic retention time (HRT) of 5 days, organic loading rate (OLR) of 12-15 kg volatile solids (VS)/m^3 d. The temperature was controlled by means of a thermostatic jacket. The reactor was operated at 37 °C. Before the fermentation, a thermal pre-treatment (72°C, 48 h) was applied to the feedstock, in order to foster the organic matter solubilization. After this time, the reactor temperature was decreased and maintained at 37°C for five days. The solid/liquid separation stage consisted of two stages: a) a coaxial centrifuge equipped with a nylon filter bag of 5.0 μm porosity, necessary for solids removal, followed by b) 0.2 μm porosity ultrafiltration ceramic membrane. Anaerobic co-digestion was conducted in a 230 L working volume stainless steel CSTR (AISI-304). The reactor was equipped with a mechanical anchor stirrer and the temperature was maintained at 37 °C by hot water recirculation through an external jacket (HRT of 15 days; OLR of 3.0-3.5 kg VS/m^3 d). The inoculum was collected from the contiguous 2000 m^3 full-scale anaerobic digester and it was acclimatized for at least 2 HRTs.

2.2 Aerobic steps: MMC selection and PHA accumulation

In the aerobic line, the culture selection was conducted in a reactor of 100 L working volume. Dissolved oxygen (DO) concentration was maintained at a maximum of 8.0 mg O_2/L with linear membrane blowers (Bibus EL-S-250), which also allowed the complete stirring of the mixed liquor. DO concentration, oxidation reduction potential (ORP), pH and temperature were constantly monitored in real time by immersion probes (Hamilton®) and online signals were acquired through a programmable logic controller (PLC; myRio Labview by National Instrument®). Temperature was regulated by an immersion heater and maintained between 25 and 28 °C in both aerobic units. The operating cycles of the SBR were managed and controlled by the PLC. The SBR was operated with an intermediate OLR (4.0 g COD/L d) with a real substrate for 45 days, by maintaining the same HRT or SRT (1.0 d) and cycle length (12 h). The PHA accumulation reactor was operated in fed-batch mode with the same equipment as the selection reactor; the working volume was 80-120 L, depending on the substrate availability. The permeate of the liquid VFA-rich stream was fed by multi-spike strategy with an initial substrate/biomass ratio of 2.0 on a COD basis, in order to prevent substrate or pH inhibition phenomena (Villano et al., 2010). Over the course of each accumulation, the carbon source was progressively dosed in limited amount, in order to maintain the soluble COD concentration below 3 g COD/L.

3. Results and discussion

3.1 Acidogenic fermentation

High level of VFA compared to the soluble COD is a aspect for an effective selection process on the microbial community able to store PHA. This is particularly true with nutrient-rich carbon sources. During the whole platform operation, the fermentation process showed stable results in each batch tests. Despite of the high fermentability of the feedstock, the final pH was between 5.0 and 5.5. This was due to the buffering capacity provided by the sewage sludge, which was 70% of the total in volumetric fraction (Cabbai et al. 2016). The fermentation showed a stable VFA production in every batch, in terms of maximal concentration and distribution. The final VFA concentration ranged between 27 and 32 g COD/L; similar fluctuations were also observed for the VFA/COD_{SOL} ratio, which values fluctuated from a minimum of 0.76 up to 0.89.

The overall yield in terms of VFA production was 0.65 g COD_{VFA}/g VS (considered as initial VS before fermentation; $VS_{(0)}$). Table 1 reports the average fermented stream characteristics. The acidogenic fermentation of this mixture showed its robustness giving stable results, despite of possible feedstock variability due to the seasonality, which in turn affects the OFMSW composition much more then sewage sludge characteristics. From the technical point of view, this stage was also easy to be performed, since no inoculum was necessary, since the fermentative bacteria contained in the food waste was naturally stimulated by the mesophilic temperature. A crucial role was played by the thermal pre-treatment (before mesophilic fermentation), since the relatively high VFA content achieved was favoured by the high content of solubilized organic matter.

A recent lab-scale work (Moretto et al. 2019a) demonstrated how the fermentation process conducted on a similar substrate (food waste and sewage sludge) can be closely adapted to the selection of PHA-accumulation bacteria thanks to a thermal pre-treatment (72°C for 72 h). The latter allowed to achieve high VFA concentrations (30-40 gCOD/L) with similarly high VFA/COD_{SOL} ratios (up to 0.91). In addition, in the present study, the pilot scale fermentation process was conducted without pH control. This is also another important aspect in a perspective of future scale-up, since it allows to save cost, limiting or avoiding the use of chemicals. The VFA-rich fermented stream was utilized for the subsequent culture selection and PHA accumulation, after undergoing two solid/liquid separation units. The aim of these units (centrifuge and membrane) was the removal of all coarse solids, in order to obtain a clear VFA-rich stream and to decrease possible impurities in the final products.

3.2 Anaerobic co-digestion

Anaerobic co-digestion process was performed on a mixture of excess sewage sludge and the two overflows coming from the fermentation step; the centrifuge solid-rich fraction (or the solid cake) and the membrane retained phase. The process was started up by feeding the sewage sludge only, almost for 1.0 HRT. Then, the feeding with the two overflows started by gradually increasing their content in the feed mixture, up to an OLR of 3.5 kg VS/m^3 d approximately. The feed mixture was roughly composed by 66% of sewage sludge, 8% of solid cake and 26% of membrane retained phase, in terms of volumetric percentages. The OLR was kept at a maximum of 3.5 kg VS/m^3 d for technical reasons, since the availability of the two overflows was dependent on the operation of the centrifuge and membrane units and their volumetric capacity. The OLR was strongly affected by the solid cake contribution, due to its high solids content (235 g Total Solid/kg). The membrane retained phase, with an average solid content of 20 g TS/kg, contributed to a minor extent to the whole OLR. The mixture fed to the digester was characterized by an average TS content of 45 g TS/kg. The monitored stability parameters are reported in Table 1. The steady state period was characterized by an average gas production rate (GPR) of 1.5 ± 0.1 m^3_{biogas}/m^3 d and specific gas production (SGP) of 0.44 ± 0.02 m^3_{biogas}/kg VS. Literature studies generally report higher yields obtained with mechanically treated and pressed food waste, up to 0.65-0.82 m^3_{biogas}/kg VS, with applied OLR equal to 4.3 and 4.5 kg VS/m^3 d, respectively (Micolucci et al. 2016; Novarino et al. 2012). When the pre-treated OFMSW was mixed with sewage sludge, similar yields were obtained, close to 0.5 m^3_{biogas}/kg VS as SGP (Mattioli et al. 2017; Moretto et al. 2019b). The lower performances compared to the previous studies are most likely due to the partition of the major part of the VFA (utilized as substrate by methanogenic bacteria) into the PHA line. Comparable performances (SGP of 0.40-0.45 m^3_{biogas}/kg VS) were observed in Valentino et al. (2019b), where a similar methodology was applied for the conduction of the anaerobic co-digestion process. In this last example, the solid cake only was mixed with the excess sewage sludge.

3.3 Biomass selection and PHA accumulation

A single long-term SBR run was performed in order to validate the performances of the enrichment of PHA-storing biomass under high-rate selection strategy (HRT and SRT equal to 1.0 day). The robust fermentation performances achieved, with high VFA (30 ± 3 g COD/L) concentrations and a high VFA/COD_{SOL} ratio (0.86 ± 0.05), ensured a good selective pressure by minimizing the growth of the non PHA-storing biomass, usually associated with the COD_{SOL} fraction other than VFA. The enrichment in PHA-accumulating microorganisms in the mixed culture was confirmed by the average specific storage rate obtained during the feast phase (qP^{feast}), equal to 375 ± 35 mg COD_{PHA}/(g COD_{Xa} h). The solid/liquid separation stages (after the fermentation step) removed most of the slowly biodegradable COD, enhancing further the specific substrate uptake rate (816 ± 41 mg COD_{SOL}/g COD_{Xa} h) and the fast establishment of famine environment after VFA depletion. The average storage yield ($Y_{P/S}^{feast}$) and average observed yield (Y_{OBS}^{SBR}) were quantified as 0.4 ± 0.02 COD_{PHA}/COD_{SOL} and 0.59 ± 0.04 COD_{VSS}/COD_{SOL} respectively. The importance of the carbon source quality (in terms of VFA level) plays a key role in determining the efficiency of the selection process, and consequently the performances obtained in the accumulation stage (Morgan-Sagastume et al. 2020). The mixture of fermented and refined sewage sludge and pre-treated OFMSW was suitable also for accumulation batches, avoiding pH inhibition phenomena through a multi-spike strategy (Montiel-Jarillo et al. 2017). An intracellular PHA content of 0.59 ± 0.03 g PHA/g VSS and a storage yield ($Y_{P/S}^{batch}$) of 0.62 ± 0.05 COD_{PHA}/COD_{VFA} were obtained after 6-7 h of accumulation (on average). The extension of the fed-batch tests did not show an increase of the accumulation performances, suggesting that the biomass reached its maximum PHA accumulation potential under these cultivation conditions. Both growth and storage responses were observed during accumulation, due to the utilization of a carbon source not deficient in nutrients. However, the storage mechanism was better stimulated and overcame the growth mechanism of substrate consumption. Overall, both selection and accumulation processes reached satisfying yields, even in comparison with what observed in other studies utilizing the same technology, and comprehensively summarized in a recent review (Estevez-Alonso et al. 2021). These results suggest that the innovative treatment of organic waste easily available in urban contexts, such as the OFMSW, can be conceived as a possible integration within the existing full-scale facilities of municipal wastewater and sewage sludge treatment.

Table 1: Main Parameters and Performances Obtained in the three anaerobic-aerobic steps

[a] Ratio between odd numbered acids precursors (3-HydroxyValerate, 3HVp) and the sum of even and odd numbered acids precursors (3-HydroxyButyrate + 3-Hydroxyvalerate; [3HB+3HV]p).

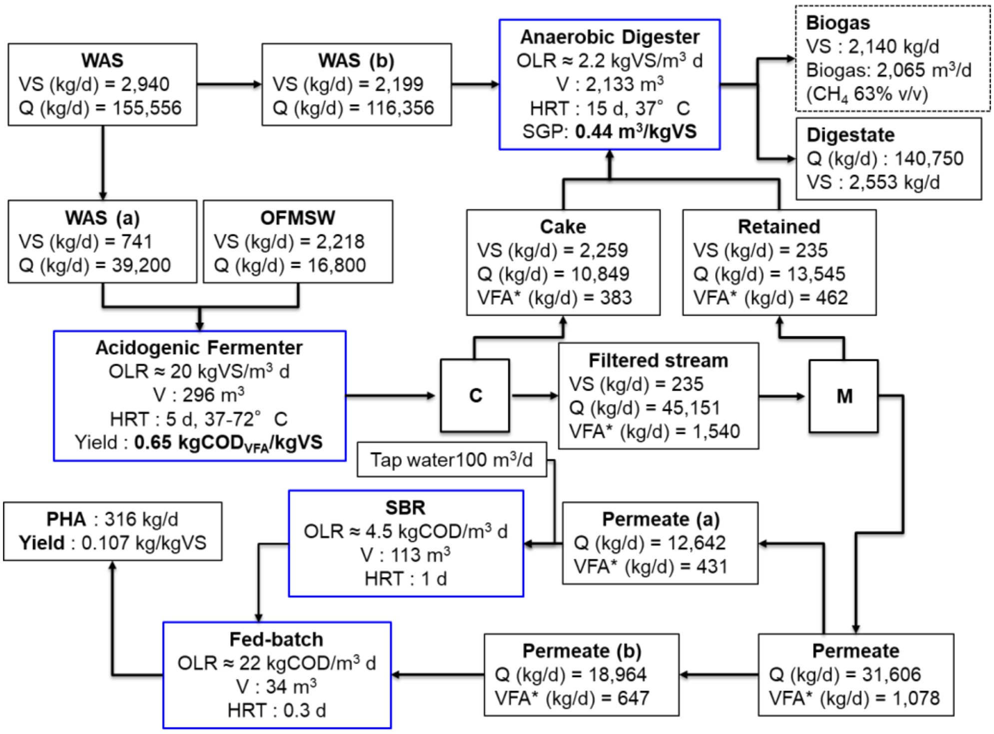
Parameters	Unit	Fermentation	Anaerobic codigestion	Selection/ enrichment stage (SBR)	Accumulation stage (fed-Batch)
COD_{SOL}	g COD/L	34 ± 3			
COD_{VFA}	g COD/L	30 ± 3	0.30 ± 0.04		
COD_{TOT}	g COD/L	70 ± 3			
COD_{VFA}/COD_{SOL}	COD/COD	0.86 ± 0.05			
$[3HV_p/(3HB+3HV)_p]$[a]	mol/mol	0.25 ± 0.02			
Yield (Y_{VFA})	$gCOD_{VFA}/gVS_{(0)}$	0.65 ± 0.04			
pH	-	5.0 ÷ 5.5	7.6 ± 0.6		
Partial Alkalinity	mg $CaCO_3$/L		1890 ± 129		
Total Alkalinity	mg $CaCO_3$/L		2903 ± 201		
Feast/Cycle Length	%			9.4 ± 0.1	
Active Biomass (X_A)	g/L			1.30 ± 0.01	
PHA content	g PHA/g VSS			0.20 ± 0.03	0.59 ± 0.03
Storage yield ($Y_{P/S}^{feast}$)	COD_P/COD_{SOL}			0.46 ± 0.02	
Observed yield (Y_{OBS}^{SBR})	COD_{Xa}/COD_{SOL}			0.59 ± 0.04	
Storage yield ($Y_{P/VFA}^{batch}$)	COD_P/COD_{VFA}				0.62 ± 0.05

3.4 Overall process yield

A whole mass balance has been evaluated for the described process configuration, applied in a full-scale platform of a hypothetical urban scenario of 70,000 Person Equivalent (PE). The inlet amount of sludge corresponds to 155,556 kg/d, indicated as “WAS” (waste activated sludge) in Figure 1. This flow rate is divided in two portions: “WAS (a)” is driven to acidogenic fermentation step (39,200 kg/d); “WAS (b)” is utilized in the anaerobic co-digestion step (116,356 kg/d) for the dilution of the two overflows. The whole OFMSW flow rate (16,800 kg/d) is driven to acidogenic fermentation. The latter step was considered to be technically feasible for the purpose of the biorefinery, and the obtained yield of 0.65 kg COD_{VFA}/ kg VS was taken into account. Three different streams from the solid/liquid separation units were obtained: the solid cake (10,849 kg/d; 21% of VS content) recovered from the unit “C”; the membrane retained phase (13,545 kg/d; 1.7% of VS content) recovered from the unit “M”; the permeate liquid stream rich in VFA (31,606 kg/d; 1,078 kg COD_{VFA}/ d) out of the unit “M” for the aerobic PHA line. The two overflows are diluted with 116,356 kg/d of excess sewage sludge, generating

an inlet anaerobic co-digester flow rate of 140,659 kg/d with a 3.3% VS content approximately (Figure 1). Based on the data obtained in the pilot scale anaerobic co-digestion reactor, such as the SGP of 0.44 m^3/kg VS, an amount of 2,065 m^3_{biogas}/d at 63% v/v CH_4 content and 140,750 kg/d of digestate have been estimated.
The yields and the flow rate partitions in each single polit units have been taken into account for the quantification of the PHA yield over the whole platform. A backward calculation began from the final PHA content in the biomass, which was equal to 0.59 ± 0.03 g PHA/g VSS at the end of accumulation, with a related PHA concentration of 2.4 g/L. Taking into account a working volume of 34 L and an HRT of 0.26 d in the fed-batch accumulation step, an overall PHA production of 316 kg/d can be obtained. Moreover, based on the VS flow rate of the initial feedstock before the acidogenic fermenter (2,958 kg/d), an overall yield of 10.7 % (kg PHA/kg VS) has been estimated.

Figure 1: Mass balance of the whole biorefinery technology chain.



4. Conclusions

The urban biorefinery developed in this study demonstrats the production of high added-value compounds (the polyhydroxyalkanoates) along with biogas. The platform gives interesting and useful data, especially related to the overall PHA yield (10.7 % wt PHA/$VS_{(0)}$), opening perspectives and possible discussions for further scale-up and economic evaluations. Overall, this approach demonstrated the potential to apply an integrated approach for the treatment of different kind of wastes through an urban biorefinery and the consequent production of bio-based products potentially exploitable on the market. The environmental concerns have been also taken into account since this biorefinery did not produce secondary waste fluxes, following the principles of the circular economy. However, each urban scenario needs to be specifically evaluated in terms of production and composition of organic waste, since the applicability of this biorefinery in a wider technology chain (starting from the waste collection to the final products) depends on the characteristics of each territorial conditions, especially on the waste management strategy and social behavior of the related citizens. A deeper study on legislative barriers, consumers' different attitude and marketing strategies is also another point for the technology evolution and its stabilization for the spreading of the bio-products in the market in an economically sustainable way.

Acknowledgments

This work was supported by the REsources from URban BIowaSte" - RES URBIS (GA 7303499) project in the European Horizon 2020 (Call CIRC-05-2016) program.

References

Andersen L., Lamp A., Dieckmann C., Baetge S., Schmidt L.M., Kaltschmitt M., 2018, Biogas plants as key units of biorefinery concepts: options and their assessment, Journal of Biotechnology, 283, 130-139.

Cabbai V., De Bortoli N., Goi D., 2016, Pilot plant experience on anaerobic codigestion of source selected OFMSW and sewage sludge, Waste Management, 49, 47-54.

Colombo B., Favini F., Scaglia B., Sciarria T.P., D'Imporzano G., Pognani M., Alekseeva A., Eisele G., Cosentino C., Adani F., 2017, Enhanced polyhydroxyalkanoate (PHA) production from the organic fraction of municipal solid waste by using mixed microbial culture, Biotechnology for Biofuels, 10, 201.

Estevez-Alonso A., Pei R., van Loosdrecht M.C.M., Kleerebezem R., Werker A., 2021, Scaling-up microbial community-based polyhydroxyalkanoate production: status and challenges, Bioresource Technology, 327, 124790.

European Commission 2015, "Closing the Loop - An EU Action Plan for Te Circular Economy" http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52015DC0614.

Maina S., Kachrimanidou V., Koutinas A., 2017, A Roadmap towards a circular and sustainable bioeconomy through waste valorization, Current Opinion in Green and Sustainable Chemistry, 8, 18-23.

Mata-Alvarez, J., Dosta J., Romero-Güiza M.S., Fonoll X., Peces M., Astals S., 2014, A critical review on anaerobic co-digestion achievements between 2010 and 2013, Renewable and Sustainable Energy Reviews, 36, 412-427.

Mattioli A., Gatti G.B., Mattuzzi G.P., Cecchi F., Bolzonella D., 2017, Co-digestion of the organic fraction of municipal solid waste and sludge improves the energy balance of wastewater treatment plants: Rovereto case study, Renewable Energy, 113, 980-988.

Micolucci F., Gottardo M., Cavinato C., Pavan P., Bolzonella D., 2016, Mesophilic and thermophilic anaerobic digestion of the liquid fraction of pressed biowaste for high energy yields recovery, Waste Management, 48, 227-235.

Montiel-Jarillo G., Carrera J., Suárez-Ojeda M.E., 2017, Enrichment of a mixed microbial culture for polyhydroxyalkanoates production: effect of pH and N and P concentrations, Science of the Total Environment, 583, 300-307.

Moretto G., Valentino F., Pavan P., Majone M., Bolzonella D., 2019a, Optimization of urban waste fermentation for volatile fatty acids production, Waste Management, 92, 21-29.

Moretto G., Ardolino F., Piasentin A., Girotto L., Cecchi F., 2019b, Integrated anaerobic codigestion system for the organic fraction of municipal solid waste and sewage sludge treatment: an Italian case study, Journal of Chemical Technology and Biotechnology, 95, 418-426.

Morgan-Sagastume F., Bengtsson S., De Grazia G., Alexandersson T., Quadri L., Johansson P., Magnusson P., Werker A., 2020, Mixed-culture polyhydroxyalkanoate (PHA) production integrated into a food-industry effluent biological treatment: A pilot-scale evaluation, 8, 104469.

Novarino D., Zanetti M.C., 2012, Anaerobic digestion of extruded OFMSW, Bioresource Technology, 104,44-50.

Valentino F., Morgan-Sagastume F., Campanari S., Villano M., Werker A., Majone M., 2017, Carbon recovery from wastewater through bioconversion into biodegradable polymers, New Biotechnology, 37, 9-23.

Valentino F., Moretto G., Gottardo M., Pavan P., Bolzonella D., Majone M., 2019, Novel routes for urban bio-waste management: A combined acidic fermentation and anaerobic digestion process for platform chemicals and biogas production, Journal of Cleaner Production, 220,368-375.

Villano M., Lampis S., Valentino F., Vallini G., Majone M., Beccari M., 2010, Effect of hydraulic and organic loads in Sequencing Batch Reactor on microbial ecology of activated sludge and storage of polyhydroxyalkanoates, Chemical Engineering Transactions, 20, 187-192.

Zabaniotou A., Kamaterou P., 2019, Food waste valorization advocating circular bioeconomy - A critical review of potentialities and perspectives of spent coffee grounds biorefinery, Journal of Cleaner Production, 211, 1553-1566.