Effect of Methanol-Organosolv pretreatment on anaerobic digestion of lignocellulosic materials

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Lignocellulosic materials (LMs) represent a great opportunity for the transition from a fossil fuel-based economy to a sustainable carbon-neutral bioeconomy, with anaerobic digestion (AD) being one of the most used applications (Chen *et al.*, 2008). Nevertheless, the usage of LMs in AD is still limited, due to their complex and resistant structure, which mainly consists of cellulose, hemicellulose, and lignin. Therefore, pretreatments are often required to increase the efficacy of lignocellulose hydrolysis and overcome the high recalcitrance of LMs to enzymatic attack (Ravindran and Jaiswal, 2016). Chemical and physico-chemical pretreatments are the most investigated and promising methods for lignocellulosic biomass. Their purpose is to improve the biodegradability of cellulose by removing lignin and/or hemicelluloses, increasing the accessible surface area, and reducing the degree of polymerization and crystallinity of the cellulosic component of biomass (Amin *et al.*, 2017). Organosolv pretreatment has been reported as one of the more efficient methods for lignin removal. In this pretreatment, the LMs are mixed with an aqueous organic solvent, and heated to dissolve the lignin and part of the hemicellulose, leaving the cellulose in the solid phase (Ostovareh *et al.*, 2015). Organosolv pretreatment is well integrated into the concept of biorefinery. It combines the advantages of easy recycling of the solvent and recovery of highly pure lignin fraction (Mancini *et al.*, 2018b).

In this study, almond shells (AS), spent coffee grounds (SCG), and hazelnut skin (HS) were used as lignocellulosic substrates for AD and treated with a 50% water-methanol solution, with and without the addition of sulfuric acid as a catalyst. The pretreatment was conducted at 130, 160 and 200 °C for 1 hour. Biomethane potential (BMP) batch tests were carried out under mesophilic (~ 37 °C) conditions in 250 mL serum bottles. Each bottle was filled with granular sludge as an inoculum and untreated or pretreated LMs. Distilled water was added to obtain the final solids content of 2%. Control biochemical tests, containing only inoculum and distilled water, were simultaneously carried out. All the experiments were performed in triplicate and biomethane production was recorded for 45 days. Water retention value (WRV) was measured as an indicator of porosity before and after pretreatment following the protocol described in Mancini *et al.* (2018a). The external surface of raw and treated materials was observed using a scanning electron microscope (SEM) (S2600N, Hitachi, Japan). Biogas production was quantified with a pressure reader and the gas composition was measured using a gas chromatograph (7890B, Agilent, USA) equipped with a thermal conductivity detector heated at 250 °C.

The net methane production after 45 days of AD from AS, SCG, and HS is reported in *Table 1* as an average of the triplicate. The organosolv pretreatment was particularly effective on HS (*Figure 1*). The highest methane production from HS (312.8 mL CH_4/g VS) was obtained with the catalyst addition at the lower temperature, corresponding to a 1000% improvement compared to the production obtained from the raw material. On the other hand, there was only a 10% increase in methane production when SCG was pretreated at 160 and 200°C with catalyst addition. Finally, all the applied conditions of pretreatment on AS were ineffective in terms of methane production.

The ineffectiveness on AS and low effectiveness on SCG of the pretreatment might be attributed to the low porosity of these materials. The WRV (g/g) was found to be 0.47(± 0.02) and 1.06(± 0.07) respectively for raw AS and SCG, while it was 1.41(± 0.13) for raw HS. A low WRV indicates a lower capacity of the substrates to keep water molecules in the cell wall pores and therefore also an obstacle for the solvent to penetrate the material. The WRV is used as an indicator of the accessible surface area, based on the principle that no enzyme can enter the pores of LMs if water cannot. Thus, the lower accessible surface area can potentially explain the low methane yield observed from the AD of AS even with pretreatment.

Overall, methanol-organosolv pretreatment showed to be an effective technique for enhancing the AD of HS, attaining a 10-fold increase in methane production compared to untreated HS. In particular, the lower temperature and addition of catalyst was the optimal condition for HS pretreatment. Operating at a lower temperature can offset the operation cost brought by chemical cost in the pretreatment. On the other hand, only a slight methane improvement (10%) was observed for SCG after pretreatment at a higher temperature. Opposite this, pretreatment of AS negatively affected the BMP, most likely due to the lower porosity of the raw material and loss of non-structural compounds during the washing steps.

Table 1 - Methane production from untreated and methanol-organosolv pretreated LMs in 45 days.

Pretreatment Condition	**Biomethane Production** (mL CH_4/g VS)		
	AS	**SCG**	**HS**
Untreated	23.2 ± 9.6	293.6 ± 46.3	28.7 ± 48.6
Meth-Organosolv 130 °C	8.8 ± 3.9	177.8 ± 29.8	261.5 ± 1.8
Meth(Cat)-Organosolv 130 °C	17.1 ± 3.8	274.6 ± 20.6	312.8 ± 22.9
Meth-Organosolv 160 °C	3.7 ± 3.4	244.4 ± 16.4	255.6 ± 10.5
Meth(Cat)-Organosolv 160 °C	12.0 ± 1.6	322.8 ± 43.2	300.7 ± 7.6
Meth-Organosolv 200 °C	24.8 ± 2.6	302.4 ± 41.4	273.1 ± 1.8
Meth(Cat)-Organosolv 200 °C	10.9 ± 5.8	324.2 ± 19.6	299.5 ± 12.5

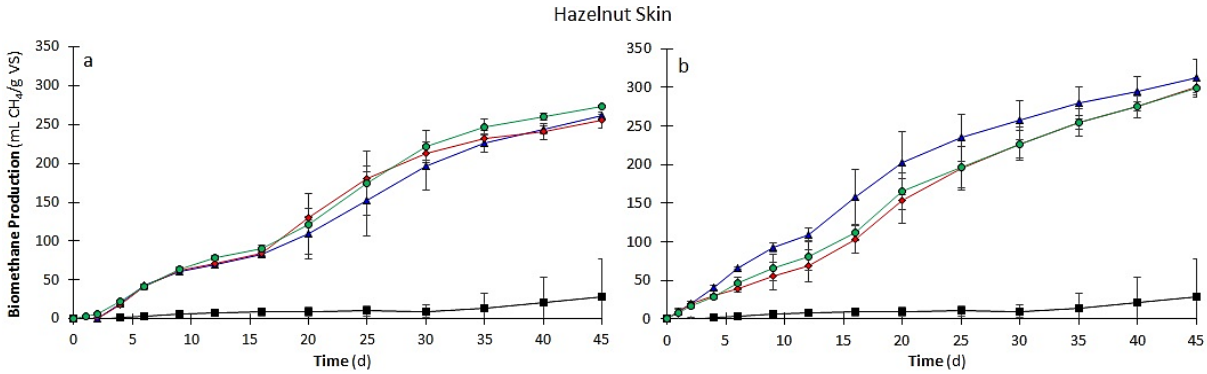

Figure 1 - Cumulative biomethane production from AD of HS: untreated (■); organosolv at 130 °C (▲), 160 °C (◆), and 200 °C (●) with (**b**) and without (**a**) catalyst addition.

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References

Amin, F. R., Khalid, H., Zhang, H., Rahman, S. u, Zhang, R., Liu, G., & Chen, C. (2017). Pretreatment methods of lignocellulosic biomass for anaerobic digestion. *AMB Express*, *7*:72. https://doi.org/10.1186/s13568-017-0375-4

Chen, Y., Cheng, J. J., & Creamer, K. S. (2008). Inhibition of anaerobic digestion process: A review. *Bioresource Technology*, *99*, 4044-4064. https://doi.org/10.1016/j.biortech.2007.01.057

Mancini, G., Papirio, S., Lens, P. N. L., & Esposito, G. (2018a). Anaerobic Digestion of Lignocellulosic Materials Using Ethanol-Organosolv Pretreatment. *Environmental Engineering Science*, *35*, 953–960. https://doi.org/10.1089/ees.2018.0042

Mancini, G., Papirio, S., Lens, P. N. L., & Esposito, G. (2018b). Increased biogas production from wheat straw by chemical pretreatments. *Renewable Energy*, *119*, 608-614. https://doi.org/10.1016/j.renene.2017.12.045

Ostovareh, S., Karimi, K., & Zamani, A. (2015). Efficient conversion of sweet sorghum stalks to biogas and ethanol using organosolv pretreatment. *Industrial Crops and Products*, *66*, 170–177. https://doi.org/10.1016/j.indcrop.2014.12.023

Ravindran, R., & Jaiswal, A. K. (2016). A comprehensive review on pre-treatment strategy for lignocellulosic food industry waste: Challenges and opportunities. *Bioresource Technology*, *199*, 92–102. https://doi.org/10.1016/j.biortech.2015.07.106