Impact of Carbon-Based Materials on the Anaerobic Digestion of Citrus Processing By-product

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Abstract: Orange peel waste holds promise for biomethane production via anaerobic digestion, though challenges such as the presence of d-Limonene, an inhibitory compound, and seasonal availability persist. In this study, ensiled OPW was used in Biochemical Methane Potential (BMP) tests to evaluate its degradability and assess the effect of carbon-based additives (i.e. granular activated carbon and biochar). Methane production was monitored over time and modelled using first-order and modified Gompertz kinetics. The highest methane yield (578 ± 59 NmL CH_4/gVS) was observed in the control, consistent with literature values for ensiled OPW. Yields from tests where additives were used ranged from 520 to 560 NmL CH_4/g_{VS}, with no significant enhancement. However, kinetic modelling indicated a slight increase in the maximum methane production rate (R_m) using an additive, suggesting an acceleration in methane production kinetics.

Keywords: Orange Peel Waste, Anaerobic Digestion, Biochemical Methane Potential, Biochar, Granular Activated Carbon

1. Introduction

Orange peel waste (OPW), a by-product of citrus processing, is rich in soluble sugars and biodegradable organic matter, making it a promising substrate for anaerobic digestion (AD) and biomethane (CH_4) production. However, its direct use is limited by the presence of d-Limonene (a well-known inhibitory compound), high moisture content, and low porosity, which can hinder microbial activity and reduce process efficiency.

Due to its strong seasonality, OPW is not consistently available throughout the year. Ensiling offers a practical preservation method, enabling storage and potentially enhancing substrate degradability by reducing d-Limonene through partial fermentation. In this study, ensiled OPW was used to assess its biomethane potential under controlled conditions (Fazzino et al., 2022).

To investigate possible process improvements, two carbon-based materials—granular activated carbon (GAC) and biochar (BC)—were tested as additives. These materials may enhance AD by adsorbing inhibitors, supporting microbial growth, and promoting syntrophic interactions such as direct interspecies electron transfer (DIET) (Fazzino et al., 2024). While these effects are well-documented for GAC, they remain under investigation for BC, which is of particular interest due to its sustainable origin from various biomass residues. This work evaluates the impact of GAC and BC on the anaerobic digestion of ensiled OPW through preliminary Biochemical Methane Potential (BMP) tests, focusing on methane yield and degradation kinetics.

2. Materials and Methods

OPW was pre-ensiled for five weeks in 80 L pilot-scale silos and subsequently used as substrate to assess the effect of carbon-based additives on methane production during AD. The carbon materials tested were GAC (supplied by NORIT) and BC (provided by AquaGreen, a company specialising in sustainable wastewater sludge treatment via pyrolysis). Four experimental conditions were investigated: OPW (control), OPW-GAC5 (OPW with 5 g/L GAC), OPW-BC5 (5 g/L BC), and OPW-BC25 (25 g/L BC). Each condition was tested in triplicate. In addition, two blank reactors containing only the inoculum were included to account for the non-specific methane production. All materials used in the BMP tests were characterised in terms of total solids (TS), volatile solids (VS), and pH. Table 1 presents the measured values.

BMP tests were performed according to an internally developed protocol, as described by Holliger et al.. Experiments were carried out under mesophilic conditions (35 ± 0.5 °C) in 1.1 L glass batch reactors, fitted with two side ports for gas sampling and a central sealed port. The inoculum was sourced from a full-scale anaerobic digestion plant (province of Reggio Calabria - Southern Italy). Methane production was measured using a liquid displacement method, as described in Pedullà et al. (2025), with biogas sampling performed three times a week.

Table 1. Characterisation of substrates and additives used in BMP tests

	TS [%]	VS [$\%_{TS}$]	pH
Inoculum	3,4±0,07	69,8±0,76	7,66
Insiled OPW	12,1±0,34	94,6±0,19	3,55
Biochar	1,9±0,08	61,5±3,61	-
GAC	1,6±0,15	58,3±3,79	-

The results of the BMP tests were modelled using two kinetic approaches: first-order kinetics and the modified Gompertz model (Calabrò et al., 2023), to describe methane production dynamics and extract key parameters related to reaction rates and microbial activity.

3. Results

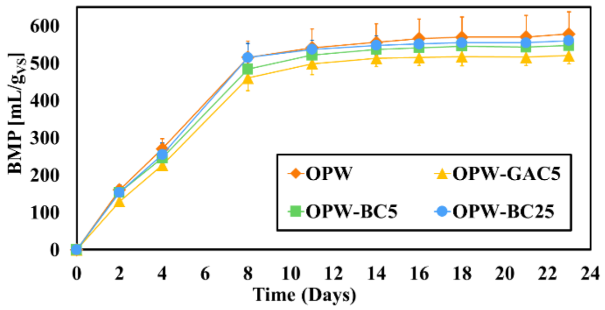

Figure 1. Methane cumulative production

Figure 1 shows the cumulative methane production for all experimental sets. From the BMP tests, a maximum methane yield of 578 ± 59 NmL CH_4/g_{VS} was observed for the control condition (ensiled OPW without additives), which aligns well with values reported in the literature for ensiled OPW, typically exceeding 500 NmL CH_4/g_{VS} (Calabrò and Panzera, 2017; Fazzino et al., 2022). Yields ranging from 520 to 560 NmL CH_4/gVS were recorded under the other experimental conditions. No significant differences were observed among the tested setups, suggesting that the addition of carbon-based materials did not negatively affect the AD process. However, no enhancement in methane production was achieved.

Table 2. Kinetics Parameters

Test	First-order			Modified Gompertz			
	B_0 $\left[\frac{NL}{g_{VS}}\right]$	k $\left[\frac{1}{d}\right]$	r^2 [%]	P $\left[\frac{NL}{g_{VS}}\right]$	λ [d]	R_m $\left[\frac{NL}{g_{VS} \cdot d}\right]$	r^2 [%]
OPW	0,60	0,19	99	0,57	0,00	0,01	99
OPW-GAC5	0,55	0,17	99	0,52	0,46	0,07	100
OPW-BC5	0,55	0,17	99	0,52	0,46	0,06	100
OPW-BC25	0,58	0,19	99	0,56	0,35	0,06	100

The parameters obtained from the kinetic analysis (Table 2) show minimal variation across the tests, with both B_0 and P ranging between 0.52 and 0.60 NL/g_{VS}. At the same time, the apparent hydrolysis rate constant k remains between 0.17 and 0.19 d^{-1}. The r^2 values are consistently high (99–100%), confirming the excellent fit of both models to the experimental data. The modified Gompertz model showed a slight advantage for the additivated reactors, due to an increase in the maximum methane production rate (R_m) from 0.01 to 0.07 NL/(gVS·d). This suggests that, although the carbon-based materials did not substantially affect the overall methane potential, they may have contributed to a faster production rate by enhancing the kinetic performance of the process.

4. Conclusions

These preliminary results confirm the high biodegradability of ensiled OPW and its suitability for anaerobic digestion. Although the addition of carbon-based materials did not enhance overall methane yield, the observed improvement in production kinetics suggests a potential benefit. Further investigation is needed under continuous or semi-continuous operating conditions to fully assess the long-term impact and practical applicability of these additives at full scale.

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