Biorefinery after the harvesting season of tomato: recovery of value-added compounds and biogas production

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Introduction

The concept of biorefinery can be a key approach towards sustainable development. In fact, it allows not only the production of value-added compounds and energy from biomass residues but also the reduction of the organic matter discarded in landfills. Portugal is the third-largest producer of tomato in the European Union (EU) with a share of 8 % of global production. However, the producers face a lack of proper management of the wastes generated after the harvesting season, namely rotten ripe tomato (TWR), green (immature) tomato (TWG) and branches of the remaining tomato plant (TWB).

This work aims to assess the extraction of phenolic compounds, the antioxidant activity and the biochemical methane production (BMP) of the referred residues, before and after the extraction process, as well as the naturally-emitted volatiles by each residue. This is an innovative study because different processes are explored based on the concepts of biorefinery and circular economy.

Material and methods

The three types of tomato residues were collected on a local farm at the end of the harvest season. Naturally-emitted volatiles were identified by solid-phase microextraction (SPME) and gas-chromatography mass spectrometry (GC/MS), and the experiments were carried out using the headspace technique at 35°C. The characterization involved the total solids (TS) and volatile solids (VS) according to APHA (1998) Standard Methods. The pH was measured in a suspension at a solid to liquid ratio of 1:10. Total chemical oxygen demand (tCOD) is determined according to standard methods (APHA, 1992). Elemental analysis (CHNS) was determined by an Elemental Analyzer NA 2500. Total Kjeldahl Nitrogen (TKN) was assessed in duplicate (Kjeldahl method, System 20, PJ Selecta). The protein (PT) content was obtained by multiplying TKN by the factor 6.25. Lipid (LP) content was evaluated, in duplicate, according to the Official Methods of Analysis of AOAC International (No. 950.54). Total lignin (LG) content was analyzed, based on NREL/TP-510-42618 Report, through the hydrolysis method. Solid-liquid extractions (SLE) were carried out in a 1 L reactor, using ethanol (100%) as a solvent in a solid to liquid ratio of 1:20 (g dried sample: mL of solvent), for 4 h at 50 ºC under agitation. After the extraction, the mixture was left to cool down at room temperature and then solid was separated from the liquid phase. The solvent was evaporated from the liquid phase and the remaining extracts were stored at 4 °C until further analysis. Phenolic content and antioxidant activity were determined in the extracts described previously using the colorimetric Folin and Ciocalteu method and the DPPH scavenging radical assay, respectively. Biochemical methane potential (BMP) tests were performed using the dried solid samples (before and after extraction). BMP tests were carried in 500 mL bottles (working volume of 20%) with an inoculum to substrate ratio (I/S) of 2, at 37 ºC. The tests were performed in duplicate and a blank was included.

Results and discussion

A number of naturally-emitted volatiles was identified in the three tomato wastes. For TWB, special attention should be given to the monoterpenes *p*-cymene, α-terpinene and α-phellandrene, that have already showed repellent activity against a tomato- whitefly. In the case of tomato fruit wastes, the TWR revealed the presence of 2-isobutylthiazole, as previously (Gaspar et al., 2019), corresponding to a tomato flavor enhancer. For the TWG, high amounts of hexenol were found, as already observed for other tomato samples (Gaspar et al., 2019).
The results of the physical and chemical characterization of the wastes studied (TWR, TWG and TWB) are summarized in Table 1.

Table 1. Physical and chemical characterization of tomato wastes studied.

Parameter	TWR	TWG	TWB	Parameter	TWR	TWG	TWB
TS (%)	6.0 ± 0.5	7.8 ± 0.1	71.4 ± 1.1	PT (%,db)	19.6 ± 0.3	17.4 ± 0.4	21.1 ± 0.6
VS (%,db)	86.0 ± 0.1	88.0 ± 0.3	80.0 ± 0.3	LP (%,db)	3.1 ± 0.4	2.8 ± 0.1	2.5 ± 0.2
pH	4.8 ± 0.1	4.0 ± 0.1	6.8 ± 0.1	LG (%,db)	7.9 ± 0.3	4.1 ± 0.9	20.3 ± 0.4
tCOD (mg O_2 gTS^{-1})	1305 ± 16	1077 ± 39	1274 ± 59	Empirical formula	$C_{28}H_{42}O_{16}N$	$C_{16}H_{25}O_{11}N$	$C_{25}H_{48}O_{18}N$
TKN (mg N/ g TS)	31.4 ± 0.5	27.8 ± 0.6	33.7 ± 1.0				

db – dry basis

Based on the high organic matter content (VS, tCOD) all residues show the potential to be valorized through biological processes. However, the lignin content (LG) is higher in the TWB, which suggests that this biowaste has less potential for methane production, at least without any pre-treatment. Overall, the three wastes present similar PT, LP and TKN content.

The extracts from the ethanol extraction were characterized in terms of their total phenolic content and antioxidant activity (Figure 1.a)). TWB extracts showed the highest total phenolic content, with a content of 26.6 ± 0.6 mg GAE/g dry extract, followed by TWR (24.4 ± 2.8 mgGAE/g dry extract) and TWG with the lowest phenolic content (7.9 ± 1.3 mgGAE/g dry extract). The phenolic content in the extract of TWR is in accordance with the literature, where 5−44 mgGAE/g extract has been reported (Silva-Beltrán et al., 2015). According to Silva-Beltrán et al. (2015), a phenolic content of 22 to 126 mg GAE/g dry extract can be achieved for TWB, depending on the weight of leaves, stems, and roots of the tomato plant. No information was found regarding the phenolic compounds in TWG. Moreover, the results presented in Figure 1.a) show that the lowest antioxidant activity is observed in TWG. High radical scavenging capacities have been determined for TWB and TWR, which is in agreement with the obtained phenolic compounds.

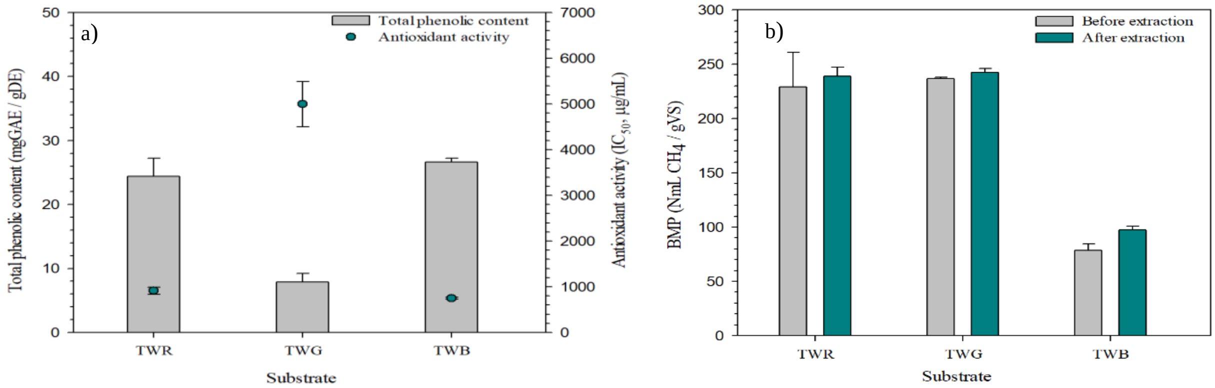

Figure 1. a) Total phenolic content and antioxidant activity of the extracts. b) Biochemical methane potential of the tomato wastes before and after the extraction step.

From Figure 1.b), it is possible to conclude that TWR and TWG are the substrates with the good potential for methane production (229 ± 32 and 237 ± 1 NmLCH_4/g VS, respectively), while the TWB shows the lowest BMP (78 ± 6 NmLCH_4/g VS). According to Gunaseelan (2007), TWR has shown a BMP from 211 to 384 mLCH_4 / gVS which is in accordance with the obtained results. For TWG and TWB, this comparison is not possible because no BMP values were found. After the extraction with ethanol, all residues showed a slight improvement in methane production, which is a very interesting result in the biorefinery context. This increase may be due to the removal of the phenolic content since according to some authors (Milledge et al., 2018) these compounds can be inhibitory for anaerobic digestion.

Overall, this work allowed to confirm that is possible to valorize tomato wastes through an integrated biorefinery concept, with the recovery of natural phenolic and antioxidant compounds without impairing their methane potential.

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