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Anaerobic digestion of orange peel in a semi-continuous pilot plant: An environmentally sound way of citrus waste management in agro-ecosystems

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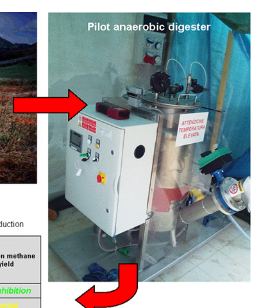
HIGHLIGHTS

- Anaerobic digestion of orange peel was carried out in a semi-continuous pilot plant.
- Experimental conditions of the tests were similar to full-scale biogas plants.
- Methane yields were higher under mesophilic conditions than in thermophilic ones.
- Partial/total inhibition was detected at high organic and essential oil loads.
- Waste conversion to biomethane increases the sustainability of citrus industry.

GRAPHICAL ABSTRACT



Effects of process operative parameters on energy production

TEMPERATURE CONDITIONS				Effect on methane yield
Mesophilic		Thermophilic		
OLR [g_{TVS} L^{-1} d^{-1}]	EOsr [mg L^{-1} d^{-1}]	OLR [g_{TVS} L^{-1} d^{-1}]	EOsr [mg L^{-1} d^{-1}]	
0.64 - 1.38	28.6 - 47.6	0.64 - 1.38	28.6 - 47.6	No inhibition
1.98	88.1	-	-	Partial inhibition
2.50	111.2	1.98	88.1	Total inhibition

Notes: OLR = Organic Loading Rates; EOsr = Essential Oil supply rates.

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ABSTRACT

The management of residues of citrus processing involves economic and environmental problems. In particular, the uncontrolled disposal of citrus processing waste near production sites can have heavy impacts on air, soil, surface water bodies and groundwater. Anaerobic digestion has been proposed as a viable alternative for citrus waste valorisation, if some problems, linked to the biochemical processes, are overcome.

Although many experimental tests have studied the inhibitory effects of the high essential oil content of orange peel on biomethanisation processes, fewer experiences have been carried out in continuous or semi-continuous pilot digesters, more similar to the full-scale biogas plants, using real orange peel.

This study has evaluated the methane production through anaerobic digestion of industrial orange peel using a pilot plant (84 L) with semi-continuous feeding at increasing Organic Loading Rates (OLR) and essential oil (EO) supply rates (EOsr) until the complete process inhibition.

Under mesophilic conditions, the highest daily specific methane yield was achieved at OLR of 1.0 g_{TVS} L^{-1} d^{-1} and EOsr of 47.6 mg L^{-1} d^{-1}. Partial inhibition of the anaerobic digestion was detected at OLR and EOsr of 1.98 g_{TVS} L^{-1} d^{-1} and 88.1 mg L^{-1} d^{-1}, respectively and the process irreversibly stopped when OLR and EOsr reached 2.5 g_{TVS} L^{-1} d^{-1} and 111.2 mg L^{-1} d^{-1}, respectively. Under thermophilic conditions, the cumulative methane production (0.12 L g_{TVS}^{-1}) was about 25% of that under mesophilic conditions (0.46 L g_{TVS}^{-1}). The thermophilic digestion was completely inhibited at lower OLR (1.98 g_{TVS} L^{-1} d^{-1}) and EOsr (88.1 mg L^{-1} d^{-1}) compared to mesophilic conditions.

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This study confirmed the suitability of anaerobic digestion of orange peel for biomethane production (provided that the right management of the process is set), in view of an environmentally sound way of agricultural residues management in agro-ecosystems.

1. Introduction

Cultivation of citrus fruits (primarily oranges) plays an important role in the agricultural sector of many countries (e.g., United States, Brazil, Mexico, China and, in the Mediterranean basin, Spain, Greece and Italy) (Martín et al., 2010; Koppar and Pullammanappallil, 2013). A share of about 30–50% of produced fruits is consumed fresh, while the remaining part is sent to industrial transformation for juice, marmalade, pectin and other foods production. Beside citrus wastewater, the industrial process produces large amounts of solid residues (peel, seeds and membranes) (Wilkins et al., 2007), which represent over 50–60% of the processed fruits (Martín et al., 2010). However, the management of citrus residues involves economic and environmental problems, due to the high amount produced (with possible air, water and soil pollution), the high processing cost and/or the low value of the final material recovered (Calabrò et al., 2016). In fact, in general, use as cattle feed is the traditional and most practised option for citrus residues disposal, but some environmental and economic concerns - such as percolation of pollutants and odours emission and insufficient request of cattle feed near the transformation industry - limit this destination.

In some contexts, there is no satisfactory mean of disposal other than dumping on land adjacent to the production sites (Martìn Santos et al., 2010; Pourbafrani et al., 2010), when more efficient and sustainable solutions lack. The dumping of citrus processing waste near production sites, as for other biodegradable waste, can have heavy impacts on air, soil, surface water bodies and groundwater. The uncontrolled rotting can lead to the emission of odours (Khoo et al., 2010) and greenhouse gases (Baur et al., 2015); these latter are produced even if citrus waste is disposed of in controlled landfills (Calabrò et al., 2015). Moreover the dumping on soil causes the release of a leachate rich in organic substances with adverse impacts not only on soil itself, but also on fresh and groundwater (Arukwe et al., 2012).

In the recent decades the use of orange peel (OP) as substrate for bioenergy production (namely bioethanol by alcoholic fermentation and biomethane by anaerobic digestion) (Ruiz and Flotats, 2014) has been suggested as a viable alternative for its management. This option not only reduces the environmental drawbacks linked to pollution from poor waste-management practices, but also allows the increase of citrus processing company profits by the recovered energy sale (with or without subsidies) (Zema, 2017). Theoretically, the high organic content of OP mainly consists of various soluble and insoluble carbohydrates and this makes this substrate suitable for biogas or ethanol production (Pourbafrani et al., 2010; Koppar and Pullammanappallil, 2013). In general, from the energy yield perspective, ethanol production as OP valorisation option is not as efficient as methane production: the biochemical methane potential (BMP) of citrus peel is 1.5–2 times higher than the values obtained with bioethanol; in addition, by using co-digestion strategies, other by-products could be co-treated with the orange waste, thereby contributing to integral waste management within the producing area (Ruiz and Flotats, 2014). Thus, anaerobic digestion is the most promising process for energy conversion of this residue (Calabrò et al., 2016).

The main obstacle for OP use as a substrate for biogas production is its high content of essential oils (EO) (up to 0.4–0.5% w/w) (Kimball, 1999; Martín et al., 2010). This compound, mainly composed of D-limonene (86–96%) (Ruiz and Flotats, 2014), is highly toxic for microorganisms and thus EO presence decreases the biogas yield of OP anaerobic digestion (Mizuki et al., 1990; Pourbafrani et al., 2010; Ruiz and Flotats, 2014). Various processes have been developed to increase the energy efficiency of OP anaerobic digestion, such as several pre-treatments (e.g. size reduction, steam distillation, hexane extraction, addition of enzymes, steam explosion and combination of steam explosion and dilute acid hydrolysis) to remove D-limonene before the substrate is digested (Koppar and Pullammanappallil, 2013). However, these pre-treatments are in several cases expensive and thus unsustainable from an economic point of view. Dilution of EO present in OP by co-digestion with other feedstocks is another option.

Scientific literature reports many experimental tests of OP anaerobic digestion, but the experiments made on citrus co-digestion with other substrates are few (Mandal and Mandal, 1997; Martín et al., 2013). The important review of Ruiz and Flotats (2014) reports measurements of biogas and methane yields and the effects of EO concentration on citrus peel biomethanisation, as performed by several Authors; in summary, a wide range of inhibition limits for D-limonene are reported for anaerobic digestion: 24 mg L^{-1} d^{-1} (Srilatha et al., 1995); 34 mg L^{-1} d^{-1} (Forgács et al., 2011); 65 μL L^{-1} d^{-1} (Mizuki et al., 1990); 75–95 mg L^{-1} d^{-1} (Lane, 1984); 192 mg L^{-1} d^{-1} (Akao et al., 1992). The same authors found an inhibitory effect of EO at a concentration of about 200 mg L^{-1} during BMP experiments (Ruiz and Flotats, 2016). With regards to the effects of OLR on methane production, under mesophilic conditions, Lane (1980), Mizuki et al. (1990) and Srilatha et al. (1995) reported an inhibition limit between 2.0 g L^{-1} d^{-1} of Total Solids (TS) - corresponding to 1.9 g L^{-1} d^{-1} of Total Volatile Solids (TVS) - and 2.5 g L^{-1} d^{-1} of TVS; under thermophilic conditions, according to Kaparaju and Rintala (2006) the OLR that makes the anaerobic process unstable is 5.6 g_{TVS} L^{-1} d^{-1}.

Beside the evident dispersion of data due to the different conditions adopted for the processes (e.g., the different inocula), the majority of these experiments have been carried out through laboratory batch tests and often by adding externally D-limonene to the substrate or removing EO before digestion. For instance, Calabrò et al. (2016) evaluated the effect of increasing the concentration of orange essential oil (up to 2 g L^{-1}), reporting methane yields up to 0.37 NL g_{TVS}^{-1} in mesophilic and 0.30 NL g_{TVS}^{-1} in thermophilic conditions; moreover, the same Authors observed that D-limonene is quantitatively transformed in *p*-cymene, but that other removal mechanisms could be present, as, for example, volatilization. With regards to specifically EO removal before digestion, many treatments, such as distillation, aeration, solid state fermentation, biological removal, steam explosion, solvent extraction, were investigated, in order to evaluate the influence of EO reduction on anaerobic digestion performance (Ruiz and Flotats, 2014): for example, under mesophilic conditions, Lane (1984) found that an OLR up to 3.5 g_{TS} L^{-1} d^{-1} can be adopted. Considering that TVS are about 95% of TS (Ruiz and Flotats, 2014; Martín et al., 2010), this OLR corresponds to about 3.3 g_{TVS} L^{-1} d^{-1}.

However, very few experimental tests of OP anaerobic digestion have been carried out in continuous or semi-continuous pilot digesters, which are (more similar to the full-scale biogas plants), using real OP. To fill this gap, this study aims to evaluate the methane production through anaerobic digestion of industrial orange peel using a pilot plant (84 L) with semi-continuous feeding. More specifically, the specific methane yields have been measured under mesophilic and thermophilic conditions at increasing OLR and EO concentrations until complete process inhibition; the limits of OLRs and EO supply of our study have been compared with literature data.