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Effect of the concentration of essential oil on orange peel waste biomethanization: Preliminary batch results

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ABSTRACT

The cultivation of orange (*Citrus* × *sinensis*) and its transformation is a major industry in many countries in the world, it leads to the production of about 25–30 Mt of orange peel waste (OPW) per year. Until now many options have been proposed for the management of OPW but although they are technically feasible, in many cases their economic/environmental sustainability is questionable. This paper analyse at lab scale the possibility of using OPW as a substrate for anaerobic digestion. Specific objectives are testing the possible codigestion with municipal biowaste, verifying the effect on methane production of increasingly high concentration of orange essential oil (EO, that is well known to have antioxidant properties that can slower or either inhibit biomass activity) and obtaining information on the behaviour of D-limonene, the main EO component, during anaerobic digestion. The results indicate that OPW can produce up to about 370 L_n CH_4/kg VS in mesophilic conditions and up to about 300 L_n CH_4/kg VS in thermophilic conditions. The presence of increasingly high concentrations of EO temporary inhibits methanogenesis, but according to the results of batch tests, methane production restarts while D-limonene is partially degraded through a pathway that requires its conversion into *p*-cymene as the main intermediate.

1. Introduction

The cultivation of orange (*Citrus* × *sinensis*) and its transformation is a major industry in many countries in the world. According to official data, orange is the most cultivated fruit in the world and in 2010 more than 68 Mt were produced. Brazil is the first producer, followed by United States, India, China, Mexico, Spain, Egypt and Italy; all these countries have a production higher than 2 Mt per year and cover more than 60% of the world production (FAOSTAT, Statistical database of the Food and Agriculture Organization of the United Nations, 2014).

About 70% of the oranges produced are transformed into juice, marmalade and other foods, leading to the production of an amount of citrus peel waste that represents about 50–60% of the processed fruit (Martìn et al., 2010). It can be therefore assessed that orange transformation industry produces about 25–30 Mt of orange peel waste (OPW) per year. OPW is composed of the peel, seeds and membrane residues (Wilkins et al., 2007) and contains water (75–85% w/w on average), mono and disaccharides (glucose, fructose, sucrose; 6–8% w/w on average), polysaccharides (pectin, cellulose and hemicellulose; 1.5–3% w/w on average), and is characterized by a very low pH (3–5) and a significant presence of essential oil (EO) composed mainly by D-limonene (83–97% w/w, Bicas et al., 2008).

Although several processes for the valorisation of OPW have been proposed (production of fertilizers, pectin, ethanol, EO, cattle feed, absorbent material¸ see Martìn et al., 2010; Ruiz and Flotats, 2014), due to the high amount produced and to the high processing cost and/or low value of the final material recovered, a fully satisfactory solution has not been established yet. Unfortunately, in many countries, OPW is normally dumped near production sites and sometimes partially used as cattle feed. However this management solution cause many drawbacks (e.g. liquid emissions to soil, odour problems).

A very promising solution could be the use of OPW as substrate for biomethane production by anaerobic digestion. Anaerobic digestion is a very efficient biochemical process to convert biomass into gaseous biofuel, thanks to the mild operating conditions and the very low anabolic energy requirements. It is also applicable

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to a wide range of natural complex organic residues (Calabrò et al., 2015; Liotta et al., 2015), only lignin being recalcitrant to anaerobic digestion (Sambusiti et al., 2012; Pontoni et al., 2015).

In addition to the production of biogas rich in methane that is a renewable source of energy, anaerobic digestion prevents landfilling of biodegradable organic materials (e.g. food and agro-industrial waste) thus reducing methane emissions from landfills. Moreover, as already mentioned, in many cases agriculture waste are disposed of in an uncontrolled way near production site potentially leading to several problems (e.g. odour, methane and ammonia emission, fresh and groundwater pollution).

Amendment of soil with anaerobically digested sludge can reduce the need for chemical fertilizers, improve plant growth, reduce soil erosion and nutrient run-off, alleviate soil compaction, and help soil's water retention.

The main issue for the use of OPW in biologic processes is its high content of EO that, being mainly constituted of D-limonene, a well known antioxidant, can inhibit biomass activity (see Ruiz and Flotats, 2014; Forgács et al., 2011; Martìn et al., 2010; Mizuki et al., 1990; Lane, 1980). However, according to literature (Ruiz and Flotats, 2014; Lane, 1980) essential oils present higher antimicrobial activity than that of their major components taken together. A clear threshold value for inhibition has not been detected, with reference to orange essential oil, data adapted from Ruiz and Flotats, 2014 for different microorganisms ranges from about 0.4 mg/mL to about 10 mg/mL.

The EO content in oranges (referred to the whole fresh fruit) is in the range 0.3–0.8% w/w (Martìn et al., 2010; Kesterson and Braddock, 1975) leading to a potential content in OPW up to about 1.5% w/w.

Moreover, in almost all modern industrial plants, EO is extracted as a by-product of orange juice production, mostly to not alter the juice taste; residual EO content in OPW is, therefore, function of the transformed cultivar and of the processing technology adopted (e.g. with or without efficient EO extraction). The average value of residual EO content in OPW is, hence, probably close to 0.4–0.5% w/w in wet weight but it is lower for state-of-the-art plants (down to 0.1–0.2% w/w) while it is higher for OPW coming from plants with less efficient EO recovery (Martìn et al., 2010; Kimball, 1999).

Compared to other substrates, little information on anaerobic digestion of OPW is available from scientific literature until now, however some important information can be gained. The important review by Ruiz and Flotats (2014), reports that the biochemical methane potential (BMP) of citrus peel is in the range 460–640 L_n CH_4/kg VS, Forgács et al. (2011) obtained a specific methane production with respect to the volatile solids added to the system with substrate of about 537 L_n CH_4/kg VS in thermophilic conditions (55 °C) using OPW after removing the EO by steam explosion. Martìn et al. (2010) obtained about 230 L_n CH_4/kg VS in mesophilic conditions (37 °C), 332 L_n CH_4/kg VS in thermophilic conditions (67 °C) using OPW after removing the EO by steam extraction. Kaparaju and Rintala (2006) in batch experiments in thermophilic conditions reported a production of about 490 L_n CH_4/kg VS while in a semi-continuous experiment the production rate increased to 600 L_n CH_4/kg VS. Gunaseelan (2004) measured the BMP of various citrus waste, 455 and 502 L_n CH_4/kg VS were obtained respectively for orange peels and pressings in mesophilic conditions (35 °C) while in similar conditions 486, 433, 494 L_n CH_4/kg VS were respectively obtained for mandarin peels, pressings and rotten fruits.

Scope of this research is to investigate at lab scale:

- co-digestion of OPW with kitchen waste (i.e. biowaste), as due to seasonality of OPW production and in case of limited production, an interesting disposal option would be to co-digest them in municipal anaerobic digestors treating separately collected biowaste (Esposito et al., 2012; Scaglione et al., 2008). Moreover co-digestion could limit adverse effects of D-limonene on anaerobic biomass;
- the effect of increasing concentrations of orange EO (up to 2000 mg/L) on the anaerobic digestion of OPW only. This condition, although probably not real, was chosen as extreme condition, to properly understand the inhibition mechanism and the EO influence on kinetic and on the overall biodegradability of OPW. In fact in the hypothesis that EO is non-biodegradable and in lack of other removal mechanisms (e.g. volatilization, adsorption) in principle its concentration increases in continuous processes;
- the D-limonene behaviour during the anaerobic digestion of OPW only, focusing on its degradation/conversion pathways.

Batch experiments were carried out, in both mesophilic and thermophilic conditions, to measure biochemical methane potential at 30 days (BMP_{30}).

D-Limonene degradation was evaluated by measuring its residual concentration in the liquid bulk at the end of the methane production, while the formation pathway and kinetics of its degradation products are followed through the developing of the process.

2. Materials and methods

2.1. Substrates

The amount of OPW needed for the entire research was produced in the laboratory of Università di Reggio Calabria by squeezing fresh mature oranges in order to obtain a residual similar to that of industrial plants, then it was characterized in terms of total solids (TS), volatile solids (VS), chemical oxygen demand (COD) (Table 1) according to conventional standard methods (APHA et al., 2005). In order of controlling as accurately as possible the amount of EO present in the experimental systems, OPW was then treated to extract EO by microwave steam diffusion using the procedure suggested by Farhat et al. (2011). Residual EO concentration at the end of extraction was 0.971 g/kg TS (equivalent to about 5% w/w of the average value of residual EO in OPW from industrial plants).

The processed OPW was dried in an oven (Binder ED 115) at 50 °C and then milled using a cutting mill (Fritsch Pulverisette 15) until obtaining a final particle size <1 mm, the pulverised OPW was then kept at 4 °C before use. Then ready substrate was shipped to the laboratory of the Politecnico di Milano. These pretreatment procedures, although quite intense, were necessary in order to obtain a homogeneous, stable substrate for the batch experiments to be carried out in the two laboratories.

Biowaste needed for testing the codigestion with OPW was obtained by mixing various types of household food waste representative of Italian situation (Porqueddu et al., 2013). After the addition of the different components, the biowaste mixture was grinded by using a commercial blender, lyophilized (SCANVAC Coolsafe 55-4, – 55 °C) and characterized in terms of TS, VS, COD

Table 1
Characteristics of OPW and biowaste.

Parameter	Fresh OPW	Lyophilized biowaste
Humidity [% w/w]	75.1	5.0
TS [% w/w]	24.9	95.0
VS [% TS]	95.8	91.4
COD [mg O_2/g TS]	1035.0	1189.0

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