Journal of Environmental Management 215 (2018) 366–376

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Biomethanization of citrus waste: Effect of waste characteristics and of storage on treatability and evaluation of limonene degradation

Adriana Maria Lotito[*, 1], Marco De Sanctis, Carlo Pastore, Claudio Di Iaconi[**]

Water Research Institute, National Research Council, viale De Blasio 5, 70132 Bari, Italy

A R T I C L E   I N F O

Article history:
Received 12 November 2017
Received in revised form
12 March 2018
Accepted 13 March 2018

Keywords:
Citrus peel waste
Anaerobic digestion
Limonene inhibition
Linalyl acetate
Storage

A B S T R A C T

This study proposes the evaluation of the suitability of mesophilic anaerobic digestion as a simple technology for the treatment of the citrus waste produced by small-medium agro-industrial enterprises involved in the transformation of *Citrus* fruits. Two different stocks of citrus peel waste were used (i.e., fresh and stored citrus peel waste), to evaluate the influence of waste composition (variability in the type of processed *Citrus* fruits) and of storage (potentially necessary to operate the anaerobic digester continuously over the whole year due to the seasonality of the production) on anaerobic degradation treatability. A thorough characterization of the two waste types has been performed, showing that the fresh one has a higher solid and organic content, and that, in spite of the similar values of oil fraction amounts, the two stocks are significantly different in the composition of essential oils (43% of limonene and 34% of linalyl acetate in the fresh citrus waste and 20% of limonene and 74% of linalyl acetate in the stored citrus waste). Contrarily to what observed in previous studies, anaerobic digestion was successful and no reactor acidification occurred. No inhibition by limonene and linalyl acetate even at the maximum applied organic load value (i.e., 2.72 $gCOD_{waste}/gVS_{inoculum}$) was observed in the treatment of the stored waste, with limonene and linalyl acetate concentrations of 104 mg/l and 385 mg/l, respectively. On the contrary, some inhibition was detected with fresh citrus peel waste when the organic load increased from 2.21 to 2.88 $gCOD_{waste}/gVS_{inoculum}$, ascribable to limonene at initial concentration higher than 150 mg/l. A good conversion into methane was observed with fresh peel waste, up to 0.33 $l_{CH_4}/g_{COD_{removed}}$ at the highest organic load, very close to the maximum theoretical value of 0.35 $l_{CH_4}/g_{COD_{removed}}$, while a lower efficiency was achieved with stored peel waste, with a reduction down to 0.24 $l_{CH_4}/g_{COD_{removed}}$ at the highest organic load.

1. Introduction

Citrus industry plays an important role in world economy: the world production of *Citrus* accounted for 137.8 million tonnes in 2014, with an increasing trend with respect to previous years; European production amounted to 11.3 million tonnes, with the leading producers being Spain (62%), Italy (24%) and Greece (9%) (FAOSTAT, 2017). About 70% of the produced *Citrus* is processed and transformed (Siles et al., 2016): beside the main product represented by orange juice, other important goods are produced, e.g. essential oil, citrus honey, marmalade (Siles López et al., 2010). The transformation of *Citrus* fruits (orange, lemon, lime, grapefruit, etc.) generates wide amounts of waste, as about 50–65% of the processed fruit becomes citrus peel waste (composed of peel, seeds and membrane residues), that has to be correctly processed to avoid serious environmental pollution (Mandalari et al., 2006; Wilkins et al., 2007).

Usually, such a residue is disposed on agricultural land (directly or after composting); other disposal routes include the production of cattle feed and burning (Martín et al., 2010; Siles López et al., 2010). However, in order to reduce water content, it is necessary to press the peel using calcium hydroxide as binder: as a result, a highly polluted wastewater is obtained, characterized by high organic content and high alkalinity (Martín Santos et al., 2010). Moreover, the amount of orange peel that can be added to the feed is limited, as high doses can cause rumen parakeratosis, a disease of cattle digestive tract, and it is necessary to pay great attention

* Corresponding author.
** Corresponding author.
E-mail addresses: adriana.lotito@libero.it (A.M. Lotito), claudio.diiaconi@ba.irsa.cnr.it (C. Di Iaconi).
[1] Permanent address: Regione Puglia, Dipartimento Mobilità, Qualità Urbana, Opere Pubbliche, Ecologia e Paessaggio, via Gentile 52, 70100 Bari, Italy.

https://doi.org/10.1016/j.jenvman.2018.03.057

during preparation and storage of feed additive to avoid the development of mycotoxins or uncontrolled methane production (Siles López et al., 2010).

Citrus waste is mostly composed of soluble and non-soluble carbohydrate polymers, which are ideal for biological conversion to biofuels such as ethanol and biogas (Forgács et al., 2012). Hence, several studies have investigated the feasibility of anaerobic digestion for orange wastes; while some of them have considered methane production from orange peel pressing liquid (Martínez-Andreu et al., 1992; Martín Santos et al., 2010; Siles et al., 2007, 2008), others have analysed peel degradation, using different types of substrates, such as comminuted (8-mm screen) peel (Lane, 1980), pelletised orange peel prepared as cattle feed (Lane, 1980), citrus peel pellets (Lane, 1984), comminuted and homogenized whole peels (Mizuki et al., 1990), peels and pressings of different *Citrus* species (Gunaseelan, 2004), juice extracted orange waste with remnants of pulp and peels from a fruit processing industry comminuted to less than 7 mm (Kaparaju and Rintala, 2006), chopped and steam distilled orange peel from orange juice manufacturing processes (Martín et al., 2010), citrus waste as it was or after steam explosion (Forgács et al., 2012), citrus waste from juice manufacturing facilities, citrus fruit cooperatives or markets with or without grinding (Ruiz and Flotats, 2016). Co-digestion has been also studied, using municipal waste (Özmen and Aslanzadeh, 2009) or other vegetable and fruit wastes (Elaiyaraju and Partha, 2012; Rajesh Banu et al., 2007) as co-substrates. Even if results cannot be directly compared, because experiments have been conducted under different conditions (mesophilic or thermophilic, batch or continuous tests, waste as it is or after some pretreatment), a strong inhibition has been typically observed due to the presence of essential oils (90% D-limonene which represents 2–3% of dry matter of citrus peel), which are known to be antimicrobial agents that may cause upset or even failure of anaerobic digesters (Martín et al., 2010a; Wikandari et al., 2015). In particular, it was reported a failure of mesophilic digestion at concentrations of 400 μl/l (Wikandari et al., 2015).

Similarly, several works have scrutinized bioethanol production from citrus wastes, using *Saccharomyces cerevisiae*, *Kluyveromyces marxianus, Candida albicans* and *Zymomonas mobilis*, achieving bioethanol production up to 90% of the theoretical value (or even higher with the bacterium *Zymomonas mobilis*) (Mishra et al., 2012; Wilkins, 2009; Wilkins et al., 2007); however, limonene was found to inhibit fermentation at concentrations of 0.05–0.20% v/v depending on treatment duration (Wilkins, 2009; Wilkins et al., 2007).

Several investigations have been carried out to solve the problem of inhibition of anaerobic digestion caused by the limonene content of citrus peels, which can consist in limonene removal, limonene recovery, or conversion of limonene into less toxic compounds (Wikandari et al., 2015). In order to increase the economic value of the waste on the one hand and to remove inhibitory compounds that limit ethanol or biogas production on the other hand, recent studies have proposed to use the biorefinery approach, that is to say the integration of biomass conversion processes and equipment to produce fuels, power and chemicals from waste biomass: in this way, it is possible firstly to extract high-value compounds (such as essential oils and pectin) and then to produce ethanol or methane from residues (mainly cellulose, hemicellulose and lignin) (Boluda-Aguilar and Lopez-Gómez, 2013; Lohrasbi et al., 2010; Siles López et al., 2010; Winrock International Institute for Agricultural Development, 1991; Zhou et al., 2008).

However, these processes are based on numerous steps that require various equipment and strong expertise to correctly run the process: such a solution, even if convenient for big industrial realities, is not suitable for small-medium enterprises, which need simpler technologies and treatment schemes. Despite ethanol has a higher market price, the production is more complicated, as hydrolysis by enzymes or chemicals is necessary to convert polymers into sugars before sugar fermentation to ethanol; on the contrary, digesting bacteria are able firstly to hydrolyse polymers and secondly to convert them into biogas (Pourbafrani et al., 2010). Hence, anaerobic digestion still represents an attractive solution for the treatment of citrus peel waste, as it is a relatively simple technology allowing the reduction of the organic load and the simultaneous generation of biogas that can be used for heating or energy production.

The objective of this study is twofold: first, the characterization of the substrate (citrus peel waste from a factory producing *Citrus* juice concentrate) to detect possible valorisation strategies and, second, the evaluation (based on biochemical methane potential tests) of the possibility to adopt anaerobic digestion for the substrate as it is, as a simple treatment solution for small enterprises. In order to take into account the variability in the type of processed *Citrus* fruits, two different stocks of citrus peel waste were used in our tests, in particular a fresh citrus peel waste and a stored citrus peel waste. This allowed to evaluate the influence of waste composition on the process as well as to verify if storage produces strong differences in treatability. In fact, as the production period is limited to about half a year, storage could be necessary to operate the anaerobic digester continuously over the whole year. Neither pretreatment nor nutrient addition have been adopted, in order to maintain treatment as simple as possible and reduce cost. Mesophilic conditions have been chosen: in fact, even if, on the one hand, thermophilic processes assure a higher methane production rate with higher organic loads and lower hydraulic retention times, on the other hand, they are also more sensitive and less advantageous in terms of energy consumption (Forgács, 2012; Nguyen, 2012; Özmen and Aslanzadeh, 2009).

2. Materials and methods

2.1. Substrate origin

Citrus peel waste was provided by a factory producing juice concentrate located in Calabria, a Southern Italian region. Several types of *Citrus* fruits are processed, including blond and blood oranges, lemons, mandarins, clementines, grapefruits, bergamots, limes. In the first step, fruits pass in a machine for rasping fruit peel, thus making essential oils pour out. Afterwards, *Citrus* fruits are pressed to obtain the juice, that is then concentrated. Citrus peel waste is the residue of such processes.

As anticipated, two different types of citrus peel waste were used in our tests, i.e. fresh and stored citrus peel waste. Both the considered samples (fresh and stored) are a mixture of different *Citrus* types. In more detail, fresh citrus peel waste is the waste directly produced from the factory and stored at −20 °C in order to preserve its characteristics, while stored citrus peel waste is the one taken from the storage tank where this type of waste is accumulated before disposal and then stored at 4 °C before tests. No precise information is available about average storage duration, as there is no well-defined schedule about waste delivery and use; nevertheless, the sample used in our study was taken towards the end of the production period (i.e., October–May) and, hence, its storage period was of the order of several months.

2.2. Substrate characterization

Substrate characterization was performed on different types of samples to analyse the following parameters: total solids (TS),