Waste Management 50 (2016) 283–289

Contents lists available at ScienceDirect

Waste Management

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

Co-treatment of fruit and vegetable waste in sludge digesters: Chemical and spectroscopic investigation by fluorescence and Fourier transform infrared spectroscopy

Maria Rosaria Provenzano [a,*], Ornella Cavallo [a], Anna Daniela Malerba [a], Francesco Di Maria [b], Mirko Cucina [c], Luisa Massaccesi [d], Giovanni Gigliotti [c]

[a] *Dipartimento di Scienze del Suolo, della Pianta e degli Alimenti, University of Bari, Bari, Italy*
[b] *LAR – Dipartimento di Ingegneria – University of Perugia, Perugia, Italy*
[c] *Dipartimento di Ingegneria Civile e Ambientale, University of Perugia, Perugia, Italy*
[d] *Dipartimento di Scienze Agrarie, Alimentari e Ambientali, University of Perugia, Perugia, Italy*

ARTICLE INFO

Article history:
Received 15 October 2015
Revised 19 February 2016
Accepted 22 February 2016

Keywords:
Anaerobic digestion
Sewage sludge
Fruit and vegetable waste
Humification parameters
Spectroscopic analysis

ABSTRACT

In a previous work co-digestion of food waste and sewage sludge was performed in a pilot apparatus reproducing operating conditions of an existing full scale digester and processing waste mixed sludge (WMS) and fruit and vegetable waste (FVW) at different organic loading rates. An analysis of the relationship among bio-methane generation, process stability and digestate phytotoxicity was conducted. In this paper we considered humification parameters and spectroscopic analysis. Humification parameters indicated a higher not humified fraction (NH) and a lower degree of humification (DH) of FVW with respect to WMS (NH = 19.22 and 5.10%; DH = 36.65 and 61.94% for FVW and WMS, respectively) associated with their different chemical compositions and with the stabilization process previously undergone by sludge. FVW additions seemed to be favourable from an agronomical point of view since a lower percentage of organic carbon was lost. Fourier transform infrared spectra suggested consumption of aliphatics associated with rising in bio-methane generation followed by accumulation of aliphatics and carboxylic acids when the biogas production dropped. The trend of peaks ratios can be used as an indicator of the process efficiency.

Fluorescence intensity of peak B associated with tryptophan-like substances and peak D associated with humic-like substances observed on tridimensional Excitation Emission Matrix maps increased up to sample corresponding to the highest rate of biogas production. Overall spectroscopic results provided evidence of different chemical pathways of anaerobic digestion associated with increasing amount of FVW which led to different levels of biogas production.

1. Introduction

The amount of sludge produced annually all over the world is expected to steadily increase reaching 13 million tons of dry matter in 2020 in the European Union (EU) (Kelessidis and Stasinakis, 2012). However, while the sludge production is on the rise, stricter environmental quality requirements and agriculture optimization are necessary in order to feed an increasing number of people. On this respect EU policy promotes the recycling of biomasses like the solid organic residue through anaerobic digestion and/or composting processes to recover bioenergy and produce alternative organic amendments (Directive 86/278/EEC; Directive 1999/31/CE; Directive 2008/98/CE).

Waste mixed sludge (WMS) is a mixture of primary sludge and waste-activated sludge produced during wastewater pollutant removal in wastewater treatment plants. Currently over 50,000 of these plants operate in the European Union and about 36,000 of them have anaerobic facilities for sludge stabilization (Bolzonella et al., 2006).

Anaerobic digestion is a process during which, in the absence of oxygen, microorganisms break down organic materials. It produces biogas and a liquid/solid residue, the so called digestate, that can be land applied as a soil amendment. Co-digestion of multiple organic wastes is often applied to increase methane production due to positive synergisms established in the digestion medium and the supply of missing nutrients by the co-substrates.

---

* Corresponding author.
E-mail address: mariarosaria.provenzano@uniba.it (M.R. Provenzano).

http://dx.doi.org/10.1016/j.wasman.2016.02.026
0956-053X/

In the last years many researchers have highlighted that co-digestion of food waste and sludge benefits from the rise in methane production and the dilution of toxic compounds (Appels et al., 2011; Edelmann, 2000; Forster-Carneiro et al., 2008; Hartmann et al., 2002; Heo et al., 2003; Kiely et al., 1997; Mata-Alvarez et al., 1992; Sosnowski et al., 2003; Gómez et al., 2006). Methane yields have been found to increase notably by increasing the fraction of food waste with respect to sludge since an important quantity of carbon is available in food waste which makes it highly degradable. However, the addition of food waste to either above or below the optimum mixing ratio can limit or even compromise the digestion performance and reduce the methane production (Heo et al., 2003; Kim et al., 2004; Purcell and Stentiford, 2006; R. Zhang et al., 2007). Since sludge is rich in proteins (30% dry matter) (European Commission, 2001), hydrolysis has been reported as the rate-limiting step in its anaerobic digestion (Dohányos et al., 2004; Mottet et al., 2010). In fact hydrolytic potential of proteins is lower than that of carbohydrates and lipids (Arnaiz et al., 2006; Bougrier et al., 2005; Eskicioglu et al., 2008; Lafitte-Trouqué and Forster, 2002; P. Zhang et al., 2007). As a result the presence of carbohydrates and lipids in food waste improves the degradation efficiency and accelerates the hydrolysis of sludge since during the process anaerobic microorganisms grow faster (Dohányos et al., 2004; Kim et al., 2003; Mottet et al., 2010) thus increasing the methanogenic potential (Pavlostathis and Giraldo-Gomez, 1991; Ponsá et al., 2008).

Fluorescence and infrared spectroscopy have been successfully applied to investigate soil organic matter (OM) (Provenzano et al., 2008), to describe changes in OM during a composting process or compost maturity (Ouatmane et al., 2000; Smidt et al., 2002), to study OM evolution during anaerobic digestion of pig slurry and successive composting of the solid fraction of digestate (Provenzano et al., 2014), and to study microbial and fungal biomass (Grube et al., 1999) and relative amounts of proteins, fats, lignins, carbohydrates in OM (Orhan and Buyukgungor, 2000) and in wastes degradation (Calderon et al., 2006; Fakharedine et al., 2006; Won et al., 2006; Pognani et al., 2010).

In a previous work (Di Maria et al., 2014) we have studied the correlations among the main process parameters and performances, particularly of bio-methane generation, process stability and agronomic quality of digestates for the co-digestion of WMS and fruit and vegetable waste (FVW) at different organic loading rates. A pilot apparatus reproducing the operating conditions of a full scale digester of an existing wastewater treatment plant was used for that aim. Main results showed beneficial effects of co-digestion of WMS and FVW both on bio-methane generation and on digestate environmental and agronomic quality. However, some aspects concerning the evaluation of the OM in digestates related to the different operating conditions needed to be further investigated for a better comprehension of process behavior and performances. In the present study we characterized digestates obtained by the above pilot apparatus by humification parameters and spectroscopic techniques such as fluorescence spectroscopy as Excitation Emission Matrix (EEM) and Fourier transform infrared spectroscopy (FTIR). The aim was to assess the OM quality and correlate it with the process conditions.

2. Materials and methods

2.1. Pilot apparatus

The pilot apparatus has been described in detail in Di Maria et al. (2014). Briefly it consisted of a 100-l continuously stirred gas tight anaerobic reactor and resembled a full-scale digester of an existing 90,000 population equivalent wastewater treatment plant. It worked at 35 ± 2 °C and at an initial hydraulic retention time of 14 days successively evaluated on the basis of the proportions of the feeding biomass. The run was started with the digestate coming from the wastewater treatment plant anaerobic digester. Successively the organic loading rate was increased adding daily a given amount of FVW with a total solid (TS) concentration of 4%.

2.2. Samples

The WMS was withdrawn from an existing wastewater treatment plant of 90,000 population equivalent at the thickener outlet and stored at 4 °C. The FVW was generated and successively frozen until further use by blending 55% potato, 28% fruit and vegetable, 10% cooked pasta, 5% bread and 2% paper (Di Maria et al., 2014).

The following samples were considered for each organic loading rate (OLR): WMS which produced digestate D at OLR = 1.46 kg VS/m^3 day; WMS + 10%FVW (digestate D10 at OLR = 1.70 kg VS/m^3 day); WMS + 20%FVW (digestate D20 at OLR = 2.1 kg VS/m^3 day); WMS + 30%FVW (digestate D30 at OLR = 2.46 kg VS/m^3 day); WMS + 40%FVW (digestate D40 at OLR = 2.80 kg VS/m^3 day).

2.3. Chemical analyses

Humic-like substances were extracted and purified as described by Ciavatta et al. (1990). The dried organic materials were extracted with a 0.1 M NaOH and 0.1 M $Na_4P_2O_7$ solution (1:50 w/v) under N_2 at 65 °C for 24 h. The suspensions were centrifuged at 12,000 rpm for 20 min, and the supernatants were filtered through a 0.45 μm membrane filter. An aliquot of the extracts was acidified to pH 2 with concentrated H_2SO_4 to separate humic (HA) from fulvic acids (FA). Coagulated HA was collected, while the supernatants containing the FA were further purified on 10–12 cm^3 of insoluble polyvinylpyrrolidone resin (Aldrich, Germany) previously equilibrated in 0.005 M H_2SO_4 (Petrussi et al., 1988). The eluate, containing the not-humified fraction (NH) was discarded. The retained fraction was eluted with 0.5 M NaOH and represented the purified FA.

Total organic carbon (TOC) was determined by the Springler and Klee wet dichromate oxidation method (Nelson and Sommers, 1996). Total extractable carbon (TEC) concentration of the filtered alkaline extract, as well as that of NH fraction, was measured by using Pt-catalysed, high temperature combustion (680 °C) followed by infrared detection of CO_2 (TOC-5000A Shimadzu Corp., Tokyo, Japan). The HA + FA C was obtained by taking the difference between TEC and NH C. Degree of Humification (DH) was calculated as DH = (HA + FA) × 100/TEC.

OM loss was calculated according to the equation described by Viel et al. (1987) and recently used also by Gigliotti et al. (2012), to describe OM loss during each anaerobic treatment cycle:

$$\mathrm{OM}_{\mathrm{loss}\%} = 100 - 100[\mathrm{X}_1(100 - \mathrm{X}_2)]/\mathrm{X}_2(100 - \mathrm{X}_1)$$

where X_1 and X_2 represent the ingestate and digestate ash content for each cycle, respectively.

OC concentration in TEC, HA + FA and NH was corrected using the following equation:

$$\mathrm{OC}_{\mathrm{corrected\_}} = \mathrm{OC\ g\ kg}^{-1}\ (\mathrm{X}_1/\mathrm{X}_2)$$

where X_1 and X_2 represent the ash content of ingestate and digestate for each cycle, respectively. Then TOC loss was calculated:

$$\mathrm{TOC}_{\mathrm{loss}} = 100 - [(\mathrm{TOC}_{\mathrm{cd}} - \mathrm{TOC}_{\mathrm{ci}}) * 100]$$

where TOC_{cd} and TOC_{ci} represent the TOC_c in the ingestate and digestate for each cycle, respectively.