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Molecular characterization of digestates from solid-state anaerobic digestion of pig slurry and straw using analytical pyrolysis

Ornella Cavallo[a], José María de la Rosa[b,*], José Antonio González-Pérez[b], Heike Knicker[b], Daniela Pezzolla[c], Giovanni Gigliotti[c], Maria Rosaria Provenzano[a]

[a] Department of Soil, Plant and Food Sciences, University of Bari "Aldo Moro", Via G. Amendola 165/A, 70126 Bari, Italy
[b] Instituto de Recursos Naturales y Agrobiología de Sevilla, Consejo Superior de Investigaciones Científicas (IRNAS-CSIC), Av. Reina Mercedes, 10, 41012 Seville, Spain
[c] Department of Civil and Environmental Engineering, University of Perugia, Via G. Duranti 93, 06125 Perugia, Italy

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ABSTRACT

Straw and pig slurry Solid-State Anaerobic Digestion (SS-AD) was carried out in a pilot-scale apparatus using percolate recirculation technology. The digestion experiments were performed using 1, 2 and 4 recirculations per day; an additional experiment without percolate recirculation was used as control. The initial mixture and the digestates were analysed by means of chemical analyses and Pyrolysis–Gas Chromatography/Mass Spectrometry (Py–GC/MS), a direct analytical technique that allows investigating the changes in the organic matter (OM) composition of digestates and the effect of percolate recirculation frequency. Chemical analyses suggested a positive effect of percolate recirculation on OM degradation. The highest values of OM loss were found with 2 (26%) and 4 (31%) recirculation cycles per day, that also corresponded with the lowest values of the hydrophilic water extractable organic matter fraction (5.5 and 6.3% respectively). Py-GC/MS showed that the anaerobic digestion proceeded with progressive polysaccharide degradation (from c. 19% in the initial mixture to 10–8% with 2–4 recirculation cycles) and selective enrichment of lignin derived compounds (from c. 58% in the initial mixture to 67–69% with 2–4 recirculation cycles). In addition, a shift in the fatty acids distribution was observed with a decrease in the long/short chain ratio of fatty acid methyl esters. These results indicate that under our experimental conditions, percolate recirculation had a positive effect on the OM degradation. Also OM stabilization is observed with relative increases in recalcitrant lignin at the expense of the more liable polysaccharide fraction. This paper represents the first attempt to apply Py-GC/MS to evaluate the OM quality in digestates obtained by SS-AD of pig slurry and straw optimized by percolate recirculation.

1. Introduction

Anaerobic digestion (AD) is used in several European countries to treat more than 10% of the organic waste produced [1]. The final products of AD include biogas (*ca.* 65% CH_4, 35% CO_2) and an organic residue called digestate. In the near future, biogas from organic materials (*i.e.* animal manure, food waste, crop silages, *etc.*) is expected to account for at least 25% of the total bioenergy [2].

Among the different AD technologies, the most widespread operates with materials with dry matter (DM) or total solids (TS) content < 10% (wet AD). However, wet AD is not suitable to treat some wastes, such as lignocellulosic and green wastes with a solid bulk structure [3] where solid-state anaerobic digestion (SS-AD) represents a good alternative. In fact, SS-AD is used to treat different materials with TS contents > 25% that retain their shape when disposed in an open pile [4]. The SS-AD process is considered advantageous over wet AD for a number of reasons including smaller reactor volume, minimal material handling and lower energy requirements for heating along with biogas production similar to that obtained by wet AD. Moreover, SS-AD produces a final digestate easily manageable due to its low moisture content [5]. This technology currently amounts to *approx.* 54% of the total installed AD capacity in Europe, and the number of these systems has been increasing since 2005 [6].

Although SS-AD can be seen as an efficient alternative to wet AD, some drawbacks have been also found associated to the technique. For example, the use of high organic loadings, as in most of the SS-AD processes, may cause inhibition phenomena due to the accumulation of short-chain volatile fatty acids (VFAs), which results in a decrease of pH and biogas production. It is well known that, during the first step of AD, proteins, lipids and carbohydrates are transformed into amino acids, long-chain fatty acids, and sugars, respectively. All these compounds are then converted by fermentative bacteria into a mixture of short

* Corresponding author.
E-mail address: jmrosa@irnase.csic.es (J.M. de la Rosa).

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chain VFAs that are successively degraded by acetogenic bacteria to acetate, carbon dioxide, and/or hydrogen with the final step being methanogenesis. Inhibition by VFAs can be overcome by spreading the liquid fraction of the digestate, *i.e.* the percolate, on the material to be treated (approximately 10% by weight of treated waste) [4 and ref. therein].

In a preliminary study, with the aim to optimize SS-AD of straw and pig slurry by percolate recirculation, Pezzolla et al. [7] investigated the effect of recirculation frequency on biogas production, quality of the liquid fraction (*i.e.* percolate) and final digestate. They observed an increase in biogas production when using frequencies of 2 and 4 recirculations per day, especially during the first 10 days of the AD process. In fact, the increase in the frequency of percolate recirculation promoted hydrolysis in the solid fraction with the subsequent release of readily available organic compounds into the liquid fraction. These compounds were successively degraded in the percolate causing an increase in biogas production especially when the recirculation was performed 4 times per day. In addition, this accelerated degradation led to a faster mineralization of proteins in the solid fraction producing a buffer system in the percolate. The authors concluded that percolate recirculation avoids the inhibitory effects during the SS-AD, although they also indicated the need of further investigations in order to evaluate the chemical and spectroscopic characteristics mainly from the solid fraction of digestates [7].

Therefore, the aim of the present study was to investigate the effect of percolate recirculation at different frequency on the organic matter (OM) composition in the above-mentioned digestates by means of chemical analyses and analytical pyrolysis (Py–GC/MS).

The Py–GC/MS technique is widely used for the direct study of materials, which are difficult to analyze by conventional methods, one of the main advantages of this technique is the use of a small amount of sample with no prior treatment or extraction needed. Furthermore, analytical pyrolysis (Py–GC/MS) can be used as a semi-quantitative technique by calculating the relative abundance of the different compounds as percentage of total chromatographic areas.

Consequently, Py–GC/MS represents a powerful tool for analyzing organic wastes of different nature and origin. In fact, it has been applied to the characterization of compost [8,9], digested sewage sludge [10], mulched soil [11], agricultural soil and its humic fractions [12,13] and more recently to the study of fermentation processes of lignocellulosic materials [14,15]. Only a few papers have reported previously the application of Py–GC/MS to study AD processes [16,17]. Nevertheless, to the best of our knowledge, it has never been applied to study digestates obtained from straw and pig slurry, thus this study represents the first attempt to apply Py–GC/MS to evaluate the OM quality in digestates obtained by SS-AD.

2. Materials and methods

2.1. Experimental set-up

The initial mixture was composed of pig slurry and straw at a ratio of 3:1 (w/w). The three main constituents of straw are cellulose, hemicelluloses (carbohydrates) and lignin [14,17]. The animal manure is a complex solid/liquid system that contains a mixture of raw fibre, cellulose, woody parts, plants residues in various degree of decomposition, mineral materials, excretions from the digestive system such as bacteria and products of their metabolism, nitrogen compounds from the metabolism of protein and non-protein substances as well as vitamins and hormones. In general, swine manures contain about 40% of fiber (including hemicellulose, cellulose, and lignin) whereas proteins amount at about 1/4 of dry matter [18].

Inoculum, produced from a previous AD of the same substrates was added at the same amount of pig slurry to the initial mixture along with 2 l of demineralized water. Dry matter (%) of the initial mixture was 20.7 ± 1.3, volatile solids (*vs*; g/kg) were 877 ± 5.4, total organic carbon (TOC; g/kg) value was 491.0 ± 5.7 and C/N 41.3 [7]. The experimental pilot-scale apparatus was described in detail in [7]. In short, this consists of 3 polyethylene reactors of 15 l capacity equipped with a percolate recycling system and a hydraulic gasometer for biogas production measurement (Fig. 1). Two different AD technologies were compared with and without percolate recirculation, the latter as a control. The effect of different frequency of recirculation was also investigated: once (every 24 h), twice (every 12 h) and four (every 6 h) times per day. The experiment was performed under mesophilic conditions (35 ± 2 °C) during 50 days and each recirculation lasted 45 min.

At the end of each digestion process, about 100 g of samples were retrieved from each polyethylene reactor. Aliquots of these samples were used to carry out the chemical analyses. The remaining samples were thoroughly mixed in order to obtain a composite sample that was successively dried and carefully grounded in a planetary ball mill (500 rpm) to have a representative sample for each experiment. The analyzed samples were the following: the initial mixture, the digestate samples 1SS-AD, 2SS-AD, 4SS-AD obtained with 1, 2 and 4 recirculations per day, respectively, and control from the AD without percolate recirculation.

2.2. General chemical analyses

Moisture content and total *vs* were determined by weight loss upon drying at 105 °C for 24 h and subsequently heated at 550 °C in a muffle oven for 24 h, respectively. The TOC content was measured by the Springer-Klee wet dichromate oxidation method [19]. The loss of OM in the final digestates was calculated according to the equation used by Gigliotti et al. [20] to describe OM loss during composting. To determine the water-extractable organic matter (WEOM), dried samples were extracted with deionized water (1:10 w/v) and filtered with 0.45 µm membrane filter. The hydrophilic (Hi) and hydrophobic (Ho) fractions of WEOM were obtained as described in Said-Pullicino et al. [21] and the C content measured by using Pt-catalysed, high temperature combustion (800 °C) followed by infrared detection of CO_2 produced (MULTI N/C 2100/2100S, Analytikjena AG, Jena, Germany). The C content of the Ho fraction was obtained by difference between water extractable organic C (WEOC) and C concentration in the Hi fraction. Humic-like substances were obtained using the alkaline extraction as described in Ciavatta et al. [22] and recently used by Provenzano et al. [23] for digestates from sewage sludge and fruit and vegetable wastes. The alkaline extract was acidified to separate humic (HA) from fulvic acids (FA). The supernatant containing FA was purified on an insoluble polyvinylpyrrolidone column (Aldrich, Germany) and the eluate, containing the not-humified fraction (NH), was discarded. Total extractable carbon (TEC), concentration of the filtered alkaline extract, as well as that of NH fraction were measured as previously described for WEOC. The HA + FA C was obtained by difference between TEC and NH C. The degree of humification (DH) and the humification ratio (HR) were also calculated as described in Gigliotti et al. [24]. All chemical analyses were carried out in triplicate (n = 3) and standard errors (SE) were calculated and reported.

2.3. Pyrolysis-gas chromatography/mass spectrometry

Py–GC/MS was performed using a double-shot pyrolyzer (Frontier Laboratories, model 2020i) attached to a gas chromatograph (Agilent, model 6890N, Agilent, Santa Clara, CA). 1–2 mg from each composite sample were placed in small crucible capsules and introduced into a pre-heated furnace at 400 °C for 1 min. The evolved gases were then directly injected into the GC/MS for analysis. The GC was equipped with a low-polarity DB-5 (J&W Scientific) fused silica capillary column (30 m length, 0.25 µm inner diameter and 250 µm film thickness). The oven temperature was held at 50 °C for one minute and then increased up to 100 °C at 30 °C min^{-1}, from 100 to 300 °C at 10 °C min^{-1} and was