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Chemical characterization of municipal wastewater sludges produced by two-phase anaerobic digestion for biogas production

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ABSTRACT

In the present study, the chemical features of municipal wastewater sludges treated in two-phase separate digesters (one for acetogenesis and the other one for methanogenesis), were characterized by using chemical analysis, stable carbon isotope ratios ($\delta^{13}C$), HS-SPME–GC–MS, TG-DTA analysis and DRIFT spectroscopy.

The results obtained showed that sludges from acetogenesis and methanogenesis differed from each other, as well as from influent raw sludges. Both processes exhibited a diverse chemical pattern in term of VFA and VOC. Additional variations were observed for $\delta^{13}C$ values that changed from acetogenesis to methanogenesis, as a consequence of fermentation processes that led to a greater fractionation of ^{12}C with respect to the ^{13}C isotope. Similarly, the thermal profiles of acetogenesis and methanogenesis sludges greatly differed in terms of heat combustion produced. These changes were also supported by higher lipid content (probably fatty acids) in acetogenesis than in methanogenesis, as also shown by DRIFT spectroscopy.

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1. Introduction

Anaerobic digestion of organic wastewater sludge has shown to be one of the most significant processes to reduce pollution (atmospheric and terrestrial) and produce fuels (e.g. methane) [1]. Most of the models reported in the literature refer to a single-stage, anaerobic digestion process, where hydrolysis, acidogenesis, acetogenesis and methanogenesis all take place in the same reactor. In these conditions, the understanding of the chemical and biological processes acting together is extremely difficult and it has actually been approached by working on single bacterial strains or under artificial conditions [2]. To recall a pertinent example, in order to maintain an appropriate environment for microorganisms in a whole-process single reactor, volatile fatty acid (VFA) production and utilization must be balanced, since a high VFA production might lead to a reactor failure [3]. Two-stage anaerobic processes have been proposed for dividing VFA and methane forming stages, so as to optimize each stage [4–7]; this, in fact, would allow a better analysis of the chemical process involved. Every decomposition stage of sludges is characterized by quali-quantitative variations of organic carbon. These changes can be directly identified by using a multiple analytical approach similar to that applied to chemical modifications occurring in the compost [8] or soil organic matter transformation [9].

The use of thermogravimetric analysis (TGA) has recently been extended to the study of sewage sludge [10]. This technique combined with differential thermal analysis (DTA) or differential scanning calorimetry (DSC) has enabled to follow the progress of organic matter stabilization during composting processes [9–14]. The common advantage of these techniques is the simplicity of sample preparation. By combining these techniques with diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, a simple and rapid method to characterize the functional groups of composts [8,9] and soil organic matter [9,15], it is possible to obtain additional information about the structure of organic molecules involved in the transformation process.

Likewise, stable carbon isotope analysis represents a powerful monitoring tool to provide *in situ* detection of the organic matter transformation in methane [16], biodegradation of chlorinated hydrocarbons [17] and bacterial oxidation of methane [18]. Therefore, the $\delta^{13}C$ technique might improve our understanding of the transformation, utilization and stabilization of organic C during anaerobic digestion of wastes. Since a number of factors influence ^{13}C fractionation, its interpretation requires controlled laboratory experiments.

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Nomenclature

A	acetogenic digester
$\delta^{13}C$	carbon stable isotopic ratio
DRIFT	diffuse reflectance infrared Fourier transform
DTA	differential thermal analysis
HS-SPME–GC–MS	head-space solid phase microextraction combined with gas chromatography–mass spectrometry
HRT	hydraulic retention time (days)
M	methanogenic digester
$N–NH_4^+$	ammoniacal N ($g\,L^{-1}$)
SCOD	soluble chemical oxygen demand ($g\,L^{-1}$)
TA	total alkalinity ($mg\,L^{-1}$)
TG	thermogravimetric analysis
TSS	total suspended solids ($g\,L^{-1}$)
VFA	volatile fatty acids ($mg\,L^{-1}$)
VOC	volatile organic compounds
VSS	volatile suspended solid ($g\,L^{-1}$)

Several studies have highlighted the importance of VFA in methanogenesis [3]. Head-space solid phase microextraction combined with gas chromatography (SPME-GC) has been used for the determination of a variety of volatile organic compounds (VOC) in manures [19] and VFA in anaerobic processes [20]. The method is rapid and gives additional information about the anaerobic process.

In the present study, the chemical features of sludges from two separate phase digesters, one for the hydrolysis and acidification and the other one for methanogenesis, fed with municipal wastewater raw sludges, were investigated by using chemical analysis, $\delta^{13}C$ isotopic ratio, HS-SPME–GC–MS, TG-DTA analysis, and DRIFT spectroscopy, in order to detect chemical modifications that occur during acetogenesis and methanogenesis.

2. Materials and methods

2.1. Sludge

The raw sludge (influent) was obtained from a sequence of stabilization processes, carried out under aerobic–anaerobic conditions at an urban wastewater treatment plant in Bologna (Italy). The acetogenic and metanogenic inocula used in this experiment were collected from a two-phase anaerobic pilot plant fed by the same raw sludge and working in steady state conditions.

2.2. Experimental design

The entire process took place in two series of digesters fed by the same raw sludge and working in steady state conditions (Fig. 1); the first digester was for hydrolysis, acidification and acetogenesis (A), whereas the second one was for methanogenesis (M). To uniform distribution throughout the digesters, the sludges and the gas were injected through a distribution system.

The acetogenic sludge inoculum (about 1.8-L corresponding to 1.8 kg with a pH value of 4.5) was placed in each of ten 2-L total volume digesters (A1–A10) for acetogenesis. Since the first stage was operated at a hydraulic retention time (HRT) of 6 days, 300 mL d^{-1} corresponding to about 300 g d^{-1} total weight of influent were added in each acetogenic digester. The acetogenic cultures were incubated in a thermostatic chamber at a constant temperature of 25 °C ± 1.0. All acetogenic digesters (A) were continually flushed with 1.5 L d^{-1} of CO_2, resulting in a light mixing of the anaerobic culture without damage and a good CO_2 dissolution rate in the liquid phase.

The methanogenic sludge inoculum (about 1.8-L corresponding to 1.8 kg with a pH value of 7.0) was placed in each of ten 2-L total volume digesters (M1–M10) for methanogenesis. Since the second stage was also operated at a HRT of 6 days, 300 mL d^{-1} corresponding to about 300 g d^{-1} total weight of acetogenic sludge was passed from the acetogenic (A) to the corresponding methanogenic (M) digesters. The methanogenic cultures were incubated in a temperature-controlled water bath at 42 °C ± 2.0.

Agitation in methanogenic digesters (M) derives from the mixing caused by acetogenic sludges inflow and biogas produced.

During the experimental period, measurements of biogas production and composition (CH_4 and CO_2) were taken every 24 h; biogas collection and measurement was performed by water displacement method from both acetogenic and methanogenic digesters. The biogas composition was determined by using Geotech GA 2000 gas analysers (Keison Products, Chelmsford, UK). The gas output was more or less constant throughout the whole experiment and similar among replicates.

At the 6th day, the experiment was stopped and the sludges from each digester (both acetogenic and methanogenic) were freeze-dried to stop the biological activity and were subsequently analyzed.

2.3. Chemical analyses

Total C and N were measured on lyophilized sludge with an elemental analyser (CHNS-O mod. EA 1110, Carlo Erba, Italy). The percentage of C in the sample was calculated using acetanilide as a certified standard containing 71.09% of carbon.

The C isotopic ratio was measured by continuous flow-isotope ratio mass spectrometry (CF-IRMS mod. Delta Plus, Thermo Electron, Bremen, Germany).

The isotopic composition of the samples is expressed as units of $\delta^{13}C$ using Pee Dee Belemite (PDB) standard for C:

$$\delta^{13}C\,‰ = \frac{R_{sample} - R_{stdPDB}}{R_{stdPDB}}$$

where $R = {}^{13}C/{}^{12}C$.

All analyses were performed in triplicate. The reproducibility of the $\delta^{13}C$ values of the samples was better than 0.1‰ in 90% of the cases. The variation coefficient was <0.1%.

The determination of soluble chemical oxygen demand (SCOD), total suspended solids (TSS), volatile suspended solids (VSS), VFA, total alkalinity (TA), alkalinity ratio, $N–NH_4^+$ and pH was carried out according to APHA [21]. The pH, VFA and TA concentrations were measured off-line after taking samples from digesters. Total lipids were extracted using Folch's method [22].

2.4. Determination of volatile compounds by HS-SPME–GC–MS

This determination was performed according to a modified version of the method suggested by Vichi et al. [23]. About 10 mg of lyophilized sludge was weighed into a 2-mL vial and capped. A 50/30 μm divynilbenzene/carboxen/polydimethylsiloxane (DVB/Carboxen/PDMS) Stable Flex SPME fiber (Supelco, Bellefonte, PA, USA) was inserted through the septum into the vial, which was kept at 40 °C for 30 min. Vial penetration depth was set at 20 mm and, after 30 min of extraction, the SPME fiber was inserted into the injection port of the Shimadzu GC–MS–QP2010 Plus (Shimadzu, Tokyo, Japan). The injection penetration depth was set at 51 mm. The SPME fiber was desorbed at 260 °C for 10 min in the split mode. The chromatographic separation of volatile compounds was performed on a ZB-5ms fused-silica capillary column (30 m × 0.25 mm i.d. × 0.25 μm) coated with 5% phenylpolysiloxane-95% poly (dimethylsiloxane) (Phenomenex,

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