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An evaluation of stability by thermogravimetric analysis of digestate obtained from different biowastes

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Abstract

Research was carried out with the aim of monitoring anaerobic digestion processes using thermal analysis with the aid of mass spectrometry so as to define the stability of the digestate obtained. Three different systems were investigated under varying conditions. The digestion of waste sludge from a pharmaceutical industry (PI) and the digestion of cattle manure (CM) were evaluated under mesophilic conditions.

The co-digestion of a mixture of primary sludge (PS) and the organic fraction of municipal solid wastes (OFMSW) was studied under thermophilic conditions. Temperature-programmed combustion tests were carried out to investigate the degree of stabilization of samples throughout the digestion processes. The derivative thermogravimetry (DTG) profiles obtained for the mesophilic digestion of PI waste showed a decrease at low temperatures and an increase at high temperatures in the intensity of the peaks recorded as the stabilization process proceeded. These results are in accordance with those obtained by the present authors in their previous work on the mesophilic digestion of primary sludge and OFMSW. In contrast, the DTG profiles obtained from the stabilization process of CM and thermophilic codigestion of PS and OFMSW showed a reduction in peaks at high temperatures. When the stabilization products obtained from CM by anaerobic digestion and by composting processes were compared, it was observed that the composting process was capable of further decomposing materials readily oxidized at low temperatures and increasing the presence of structurally more complex substances. The evolution of the differential thermal analysis (DTA) signal recorded simultaneously showed considerable similarity to the mass/charge (*m*/*z*) signal 44 registered by the mass spectrometer. The use of mass spectrometry helped to clarify the inner workings of the digestion process.

Keywords: Anaerobic process; Thermogravimetric analysis; Biowastes

1. Introduction

The biological stabilization of organic matter has as its goal the oxidation of readily degradable materials, converting these into structurally more complex substances. Assessment of the degree of stabilization reached is a difficult task, especially when the aim is to evaluate the level of stabilization attained by different residues and through differing processes. Determination of the degree of stabilization needs to be based on a range of tests offering complementary information [1].

During the stabilization process, organic matter undergoes mineralization and conversion into humus-related, or humic, substances with a consequent reduction in the energy available for the metabolisms of micro-organisms. The use of an ignition index thus provides information regarding the combustible organic fraction and the energy released [2].

Thermal analysis has been proposed as a way of characterizing the organic matter produced in biological stabilization processes [3–6]. Monitoring the biological stabilization processes by TG-DTG would be expected to show an increase in the combustion residue of the sample linked to a decrease in the organic fraction of the sludge as the degree of stabilization increases [7].

Otero et al. [4] showed that thermogravimetric analysis can be used to monitor the stabilization process for waste-activated sludge under aerobic conditions. An association of the thermal behaviour of different sewage sludge and the stabilization process was found by Gomez-Rico et al. [8] and Font et al. [9,10]. Thermal analysis and differential scanning calorimetry (DSC) has also been used to study the degradation of organic mater during composting [11] and to evaluate compost stability [3]. Pietro and Paola [5] also proposed the use of thermal analysis to

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monitor the composting process of organic fraction of municipal solid wastes (OFMSW) and vegetable wastes, concluding that thermal analysis can be a reliable and useful tool for evaluating the transformations taking place during the composting process.

In previous study by the authors of the present paper, the anaerobic stabilization process was evaluated for the digestion of primary sludge from an urban wastewater treatment plant, for OFMSW and for a mixture of these two residues under mesophilic conditions. The results from thermal analyses showed characteristic changes in the stabilized organic matter for all three cases studied. All analyzed samples presented an increase in the amount of materials that undergo oxidation at high temperatures and a decrease in those that are oxidised at low temperatures.

Thermal analysis has also been a useful technique for the study of complex materials, such as in the evaluation of kerogen in source rocks [12] and in the characterization of soil organic matter [13–18]. Other techniques as thermogravimetry coupled to Fourier transformed infrared spectroscopy analysis and multivariate data analysis has been used to characterize soil humic substances [19]. The characterization of different decomposition stages of biowastes has also been evaluated using Fourier transform infrared (FT-IR) spectroscopy and pyrolysis-field ionization mass spectrometry (Py-FIMS), thus demonstrating that modern spectroscopy methods appear to show promise for the assessment of qualitative changes in waste materials [20].

The aim of the work reported here was to verify the use of thermogravimetric analysis as a tool for monitoring the stabilization process and to generalize its application to various digestion treatments. This experimental work studied the evolution of organic matter during the anaerobic digestion process under mesophilic conditions of waste sludge from a pharmaceutical industry and of cattle manure from a livestock farm. For the latter, the process of aerobic stabilization was likewise evaluated. Finally, the anaerobic stabilization process for a mixture of primary sludge from a wastewater treatment plant and OFMSW under thermophilic conditions was also studied.

2. Materials and methods

2.1. Experimental procedure

The experimental work consisted of three different digestion systems treating three types of waste. The wastes employed in this study were: waste sludge from a pharmaceutical industry, cattle manure, and a mixture of primary sludge (PS) and OFMSW. The heavy metals contents are lower than those imposed by legislation limits (EU directive 86/278/CEE). (Characterization was performed at the University of Leon, results not shown).

The inoculum used to start up the digestion systems came from a reactor fed with OFMSW, which had been in laboratory operation for a year. The experiments were designed with the aim of obtaining two samples from every system, corresponding to incomplete and complete digestion stages.

2.1.1. Experiment I: system for digesting waste sludge from the pharmaceutical industry

This experiment was carried out under mesophilic conditions (34 °C) in a 3 l reactor provided with a mechanical agitator. Reactor start-up was performed by adapting the inoculum to the new feed over 15 days at a low organic loading rate, subsequently establishing a hydraulic retention time (HRT) of 18 days. The system was kept running semi-continuously until a period equal to three times the elapsed HRT. Feeding was carried out once per day. The digestate obtained constituted the sample, which will be referred to as complete digestion sample.

An additional experiment was carried out to obtain the sample corresponding to the incomplete digestion stage. Digestion was performed under batch conditions for 5 days, using Erlenmeyer flasks with a working volume of 100 ml. The Erlenmeyer flasks were provided with a magnetic stirrer and immersed in a water bath at 34 °C. This experiment used digestate obtained from the reactor working under semi-continuous operation as inoculum. The volumetric ratio between inoculum and feed was five to three (5:3).

2.1.2. Experiment II: system for digesting cattle manure

The waste employed came from a livestock farm, where straw is used as bedding material for cattle, so both liquid and solid waste were gathered together. The treatment used for stabilizing cattle manure on the farm was composting. In this case, besides the samples obtained from the anaerobic digestion process, as will be further described, a representative sample from the composting process was taken to be analyzed by thermogravimetric analysis. The sample was prepared by screening through a 1 mm mesh.

The system employed for the study of mesophilic anaerobic digestion (34 °C) of cattle manure consisted of a 3 l reactor working under batch operation. This reactor was a solid state digestion reactor provided at the bottom with a system for collecting the percolate. The percolate was generated by adding 700 ml of tap water at the beginning of the trial. The liquid generated was recirculated once every day by injecting it into the top of the reactor.

The samples corresponding to the incomplete and complete digestion stages were obtained over two phases. In the first phase, reactor start-up was carried out using inoculum from the laboratory reactor digesting OFMSW. Once the solid digestate from cattle manure had been obtained, a new trial was performed using this solid digestate as the inoculum for a new reactor. In this latter case, the reactor was started up using a mixture of digestate and fresh waste in a proportion 1:1 based on wet weight. The sample, which will be referred to as the complete digestion sample was taken from the digestate obtained from this second trial. This sample was collected after 30 days of digestion, when biogas production had practically ceased. The incomplete digestion sample was taken after 5 days had elapsed from the beginning of the process.

Since the cattle manure used in this study was made up of a mixture of manure and straw, the samples taken for thermogravimetric analysis were treated through wet screening with 1 mm