

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.

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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 igni-

tion 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 matter 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

mesh sieve. The sieved fraction was collected and oven-dried, and then the obtained solid was analyzed.

2.1.3. Experiment III: system for the co-digestion of primary sludge and OFMSW

The primary sludge used in this experiment was obtained from the waste water treatment plant (WWTP) of the city of Leon in Spain. The primary sludge was concentrated to a total solid content of 6% and stored at 4 °C prior to its use. OFMSW was simulated by mixing the following ingredients: 10% banana, 10% apple, 10% orange, 35% cabbage, 25% potatoes, 8% bread and 2% paper. This mixture was ground to obtain a particle size of less than 3 mm. This mixture for co-digestion was prepared in such a way that primary sludge supplied 22% of its total solid content.

The reactor used for this system was a 1 l static reactor at 55 °C (thermophilic conditions). The HRT was 14 days and the system was kept working in semi-continuous operation until a period equal to three times the HRT had elapsed. Feeding was carried out once per day. The digestate obtained from this system constituted the sample, which will be referred to as the complete digestion sample. The sample corresponding to the intermediate or incomplete stage was obtained as in experiment I.

2.2. Analytical techniques

The digestion process was monitored using the following parameters: total solids (TS), total volatile solids (VS), gas volume, and pH, in accordance with APHA Standard Methods, 1989. For the sample of pharmaceutical industry sludge, the TS content was determined by oven-drying at 50 °C during 72 h, since at 105 °C loss of weight was continuous and thus constant weight could not be attained. Ultimate and proximate analyses for the substrates under study were carried out according to ASTM standard procedures.

Thermal analysis was performed with a TA Instruments SDT2960 apparatus registering TG and DTA measurements simultaneously. The heating rate applied to the dry samples was 25 °C/min up to 600 °C with a flow-rate of 100 ml/min of synthetic air (composition $21 \pm 1\%$ O₂ and $79 \pm 1\%$ N₂; purity $\geq 99.9994\%$). The manometric pressure was maintained at 101 kPa.

The heating rate selected for comparing the thermal degradation of samples was based on the methodology described by Otero et al. [4] and previous work published by the authors [6]. It has been observed that increments in the heating rate tend to shift the peaks recorded in the DTG profiles to the right due to the increment of the onset of devolatilization [21–24]. However, the degradation evaluated under different heating rates can be well correlated in unified models [10,23,24].

The mass-spectrometry apparatus was a Quadrupole MS (Balzers), Thermostar GSD 300 T (Pfeiffer Vacuum, D-35614 Asslar) equipped with an electron ionization source, a Faraday cup and an SEM (channeltronTM) detector. The mass range was 0–200 amu. The apparatus was used in line with the thermal analysis equipment to monitor the gas emissions obtained from the combustion process, connected through a capillary filament

Table 1
Ultimate and proximate analyses for the wastes used as substrates

Analysis (%)	Pharmaceutical industry sludge ^a	Cattle manure ^b	Mixture PS + OFMSW ^b
Ash	5.7	13.7	9.6
C	44.0	41.7	41.9
H	7.0	5.3	6.4
N	7.2	3.0	2.2
S	1.2	0.5	0.3
Cl	–	0.6	–
O	–	32.5	39.6

^a Expressed relative to the original sample. The material did not attain a constant weight at 105 °C.

^b Expressed relative to the dried material.

maintained at 200 °C. Although a full quantitative analysis could not be performed, a comparison of the intensity of the peaks obtained from different samples was made (i.e. semi-quantitative analysis) using the normalization procedure described by Arenillas et al. [25]. This normalization procedure was based on the use as the normalization factor of the maximum value of the signal recorded by the mass-spectrometry apparatus.

3. Results

Table 1 presents the results of ultimate and proximate analyses for the various types of waste used in this study. The sample of cattle manure analyzed was the original material made up of a mixture of straw and animal dejections. This sample had the lowest hydrogen content of the three residues analyzed.

Table 2 gives the results for pH, TS and VS from the samples of feedstock, the intermediate stage and the digestate obtained from the various systems evaluated. The destruction of VS noted in Table 2 refers to the destruction attained by the digestion systems relative to the feed and digestate samples. The lowest destruction of VS was obtained for the digestion system of cattle manure, since this waste was a mixture containing straw, thus explaining the lower yield of biogas relative to the total influent

Table 2
Results for pH, TS and VS from samples of feed, intermediate stage and digestate from the various systems under study

Sample	Pharmaceutical industry sludge	Cattle manure	Mixture PS + OFMSW
Feed			
TS (g/l)	60	263	60
VS (g/l)	57.8	226.2	55.2
pH	7.0	6.9	3.5
Intermediate stage			
TS (g/l)	34	198	35
VS (g/l)	26.9	170.3	25.4
pH	7.5	7.2	5.0
Digestate			
TS (g/l)	22.5	122.6	23.6
VS (g/l)	15.7	105.4	16.5
VS reduction (%)	73	53	70
pH	7.8	7.6	7.5

mass. It should be borne in mind that the configuration of this system made the addition of a bulking agent essential, so as to allow percolation of the leachate.

For all three systems under study, the pH of the samples increased as digestion proceeded. In the systems operating semi-continuously, biogas yield is expressed in terms of the volume of the reactor used ($l/l \times \text{day}$). The average amount of biogas produced by the system treating pharmaceutical waste sludge was $1.1 l/l \times \text{day}$ this value being $2.3 l/l \times \text{day}$ for the thermophilic system treating the mixture of PS + OFMSW. Biogas production by these two systems, expressed in terms of the total weight of influent solids, was 0.36 and 0.67 l/g, respectively. For the case of cattle manure digestion, where the system worked under batch conditions, gas production is expressed only in terms of the amount of total influent solids. This value was much lower than in the two former cases, being 0.14 l/g.

3.1. Experiment I: evolution of the digestion of pharmaceutical industry waste sludge

Fig. 1 presents the results obtained by thermogravimetric analysis of the different stages of the digestion process. With the mass spectrometer set up in series, the molecular species generated during the combustion process can be identified. It should be noted that each compound (ion) detected in the mass spectrometer has its own response factor and so the intensities of

each ion in different samples can be compared [8]. The chosen signals shown in Fig. 2 are those with mass/charge (m/z) proportions of 44, 64, 41 and 18. These signals confirm that the peak registered at low temperature is associated with the release of low molecular weight compounds (m/z 41), and with products generated from complete oxidation of the sample: CO_2 (m/z 44), SO_2 (m/z 64) and water (m/z 18).

DTG and DTA profiles are presented for the feed sample (Feed-PI), the sample at an intermediate stage (Int-PI) and the sample obtained from the reactor working under continuous operation (Dig-PI). From this figure a weight loss is observed around 100°C associated with a small endothermic peak in the DTA profile, caused mainly by loss of residual water. This behaviour was likewise observed in the hall set of studied samples from the different digestion systems. Dehydration around this temperature was also observed by several authors [3,5,11]. The release of water was additionally confirmed by the peak from the ion current (m/z 18) recorded by the mass spectrometer. The major water release was obtained from the Feed-PI sample, since this sample was dried at a lower temperature (50°C) due to the incapability of reaching stable weight at 105°C .

The recorded peak associated with thermal degradation at low temperatures (around 200°C) for the Feed-PI sample is worth noting in the DTG profile, as it is not associated with any energy release in the DTA profile. The signals evolved from the mass spectrometer (see Fig. 2) correlate this weight loss with the thermal degradation of the sample, mainly resulting in the release of light hydrocarbons products (m/z 41), oxidation of sulphur compounds (m/z 64), water and a small amount of CO_2 (m/z 44).

As the stabilization process proceeds, the peak registered at low temperature (Fig. 1a) shifts to the right on the temperature scale, finally becoming a peak with its maximum at 350°C for the digestate sample Dig-PI. Unlike the behaviour recorded for the samples Int-PI and Dig-PI, the DTG profile of the feed sample presents a continuous reduction in weight loss velocity at 350°C until reaching a minimum at 400°C . In the DTA profile at around 350°C , it can be observed that Dig-PI is the sample yielding the greatest energy release (Fig. 1b). This high release of energy per unit of mass can be explained by the fact that, as the stabilization process proceeds, the remaining solids have a higher degree of mineralization and hence a lower release of volatile compounds is to be expected, along with a greater oxidation of the material coupled to a greater exothermic process.

In the high temperature range, around 500°C , all three samples analyzed present a maximum in their DTG profile associated with a high energy release in the DTA signal. For sample Feed-PI, the weight loss at 500°C also results in a high release of energy, just the opposite of the behaviour of the peak registered by this same sample at low temperature, the intensity in the DTG profile of this last peak being even greater. As the anaerobic stabilization process comes to an end, the digestate obtained presents the peak with the greatest intensity in the whole profile at high temperature, together with a final sharpening of this peak.

The thermal degradation of the material studied can be grouped in three different regions as suggested by Urban and

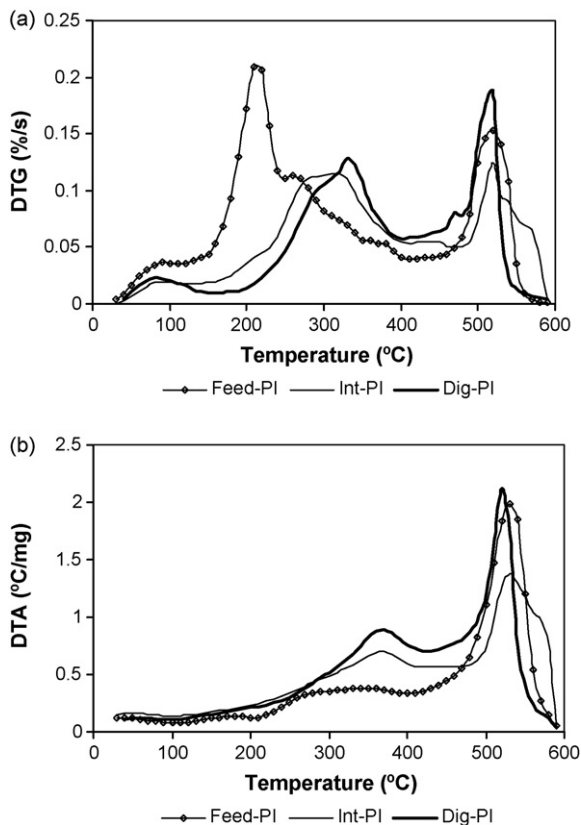


Fig. 1. (a) Evolution of the weight-loss profile in an oxidizing atmosphere (DTG). (b) Evolution of DTA signals in an oxidizing atmosphere for the digestion system of pharmaceutical industry waste sludge.

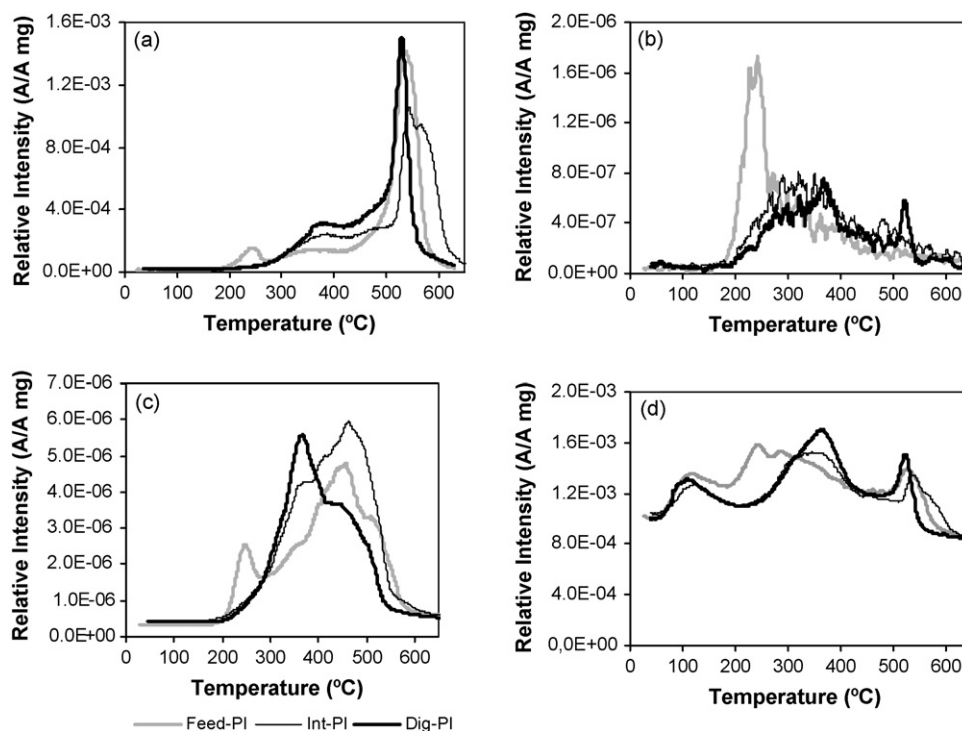


Fig. 2. Evolution of the emission profiles for m/z signals: (a) 44, (b) 64, (c) 41 and (d) 18, in an oxidizing atmosphere for the digestion system of pharmaceutical industry waste sludge.

Antal [26], and Conesa et al. [27]. This behaviour was likewise observed by several authors [3–6,9,11] and was also observed in the following digestion systems described below. The first region corresponds to the degradation at low temperature (200–300 °C) associated with biodegradable material (considering also semi-volatile compounds), the second (300 and 400–450 °C) corresponding either to organic polymers already present in the original material or generated from the stabilization process, and finally the fraction being decomposed above 450 °C related to non-degradable material.

The changes in the relative intensity of the species recorded by the mass spectrometer can be seen in Fig. 2. The m/z 44 profile develops in a similar way to that of the DTG and DTA profiles, thus verifying the similarities in CO_2 formation and the exothermic characteristic of the process. It is important to point out the redistribution of the species as stabilization progresses. Signal m/z 64 develops in a more or less uniform way for samples Int-PI and Dig-PI and the maximum emission registered by sample Feed-PI is no longer present in the following stages of digestion. The volatile compounds (m/z 41) are redistributed in such a way that their maximum is now present at 350 °C, which is where the maximum emission registered by sample Dig-PI lies. The feed sample Feed-PI presents two peaks related to the maxima recorded in the DTG profiles. As for the samples from the intermediate stage and the complete digestion stage, the evolution of their profiles presents continuity in emissions of light organic compounds, with differences in the temperature at which the maxima take place. The maximum emission for the Int-PI sample is around 500 °C, while for Dig-PI it is around 350 °C.

3.2. Experiment II: evolution of the batch digestion of cattle manure

DTG and DTA profiles for this system are presented in Fig. 3. Here, two zones are clearly differentiated in the DTG profile and thus in the associated DTA signal (disregarding the release of water, around 100 °C). The first is at 300 °C and the other between 450 and 550 °C. The intensity of the peak observed at 300 °C for the feed sample Feed-CM is the greatest and corresponds to readily oxidized materials. The intensity of this peak decreases as stabilization proceeds and no further changes are observed at the end of the process. The intensity being about the same for samples Int-CM and Dig-CM.

The Feed-CM sample yields the greatest weight loss in the low temperature range, corresponding to thermal degradation of carbohydrates [5]. However, in the DTA profile it can be observed that the energy release associated with this loss of weight is smaller than that registered for sample Dig-CM. This behaviour was also observed in the previous digestion system and as well in the following to be described, even when the feed and digestate samples present greater differences in the intensity of this peak. When a comparison is made with the other systems, it can be seen that this peak does not show great changes during the digestion process. This is in accordance with the low VS destruction noted and may also explain the low biogas yield.

In the high temperature range, from 450 to 550 °C, additional changes are noted with respect to the intensity of peaks and the temperature at which they take place, corresponding to the weight loss suffered by structurally more complex materi-

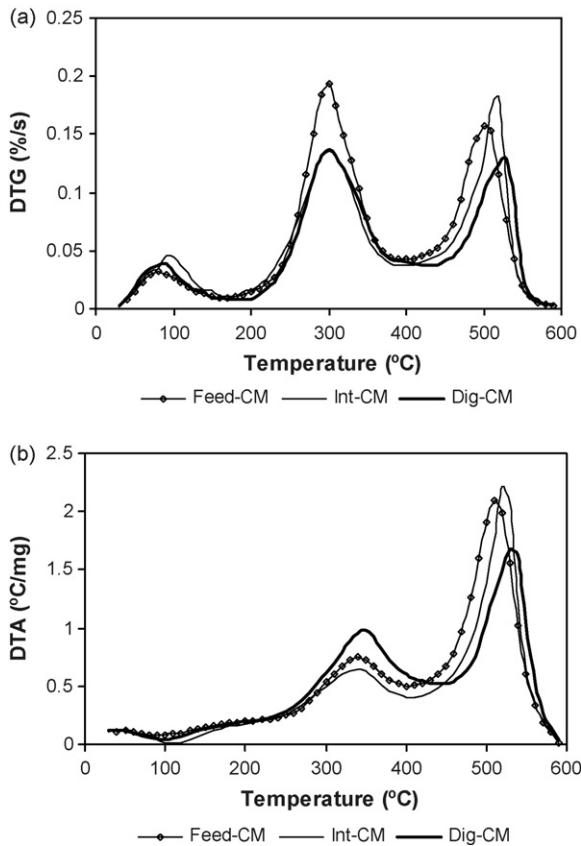


Fig. 3. (a) Evolution of the weight-loss profile in an oxidizing atmosphere (DTG). (b) Evolution of DTA signals in an oxidizing atmosphere from cattle manure digestion system.

als. The transition from the feed sample and its conversion to digestate material shows a shift to the right on the temperature scale of the high-temperature peak. In other words, the temperature at which this peak takes place is greater. It seems logical to assume that if the materials that are degraded during the thermal analysis at low temperatures cannot be further degraded under anaerobic conditions, continuing the stabilization process will lead to the degradation of other materials, namely those which are structurally more complex. As result the DTG profile for the digestate sample (Dig-CM) witnesses a reduction in the peak at high temperatures but not at low temperatures.

The signals registered on the mass spectrometer are presented in Fig. 4. The main differences can be seen for signals m/z 41 and 64. The signal representing volatile compounds shows a decrease in intensity at high temperatures as the stabilization process takes place. A slight increase can be observed for signal m/z 64 in the emission of SO_2 at around 300 °C, associated with the weight loss registered by the DTG profile of samples Int-CM and Dig-CM. The increase in the emission of SO_2 may be explained by the fact that, the total amount of mass remaining at the end of the digestion process is much lower, so materials that are not turned into biogas are concentrated in the remaining solids. Although some sulphur compounds are lost with the biogas as hydrogen sulphide and volatile sulphur compounds, from signal m/z 64 it can be seen that some others do remain in the solids. It should be borne in mind that in the previous case, although the feed sample presented a high release of SO_2 at low temperatures, there was no particular increment in the intensity of the signal for the subsequent samples (Int and Dig-sample). The profile followed by signal m/z 44 is similar to that of the DTA profile just as in the previous case.

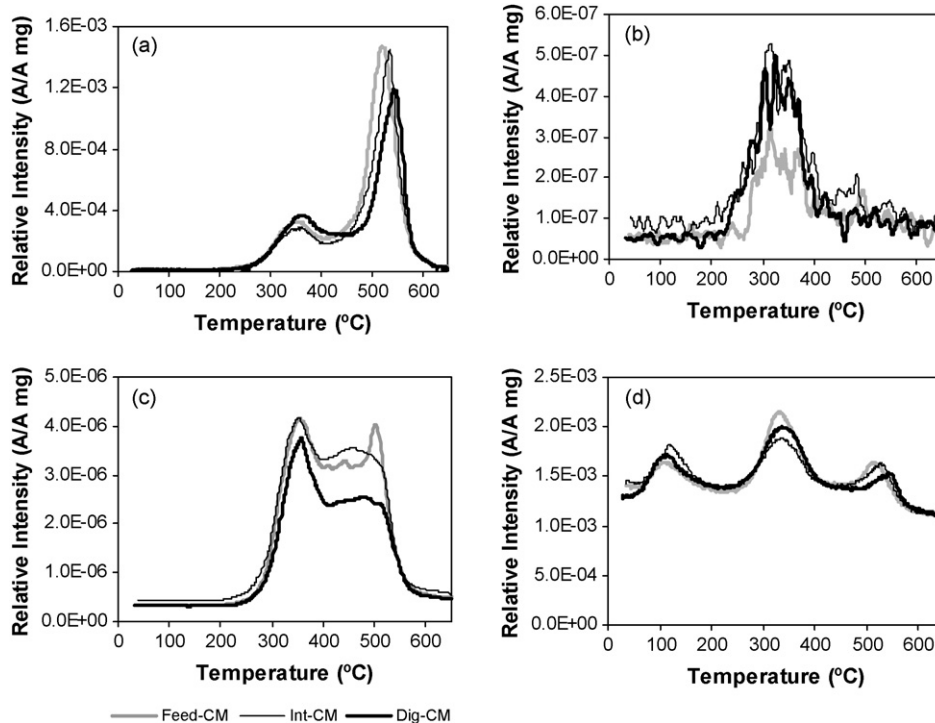


Fig. 4. Evolution of the emission profiles for m/z signals: (a) 44, (b) 64, (c) 41 and (d) 18, in an oxidizing atmosphere for the digestion system of cattle manure.

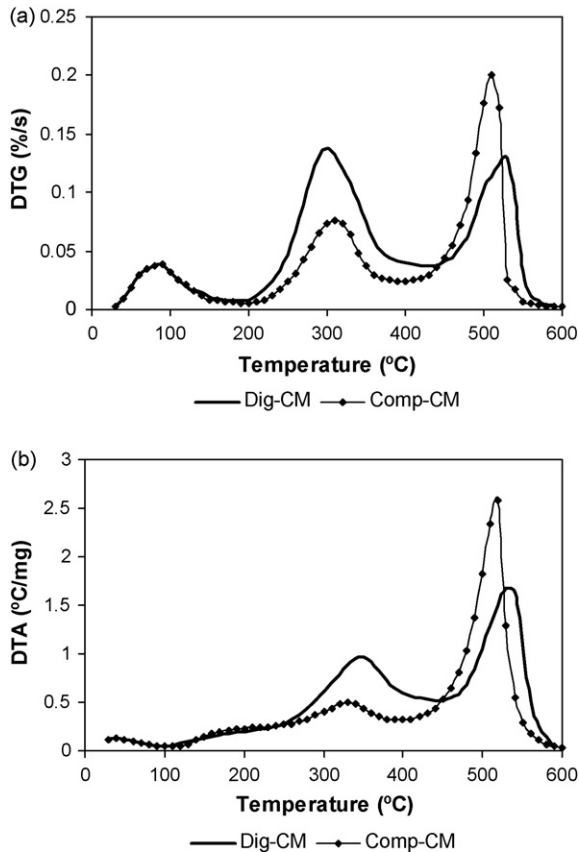


Fig. 5. (a) Evolution of the weight-loss profile in an oxidizing atmosphere (DTG). (b) Changes in DTA signals in an oxidizing atmosphere for stabilized waste obtained from digestion and composting of cattle manure.

A comparison of the profiles obtained from the waste stabilized by means of anaerobic digestion and composting can be seen in Fig. 5. The sample of compost Comp-CM was obtained from the composting process carried out at the livestock farm, while the sample of digestate corresponds to Dig-CM. From the profile it can be observed that composting is capable of a greater reduction in readily oxidized substances that were not able to oxidize under anaerobic conditions, as can be inferred from the lower intensity of the peak at 300 °C. The reduction in these materials is accompanied by an increase in structurally more complex material, this being evident through the greater intensity of the peak around 500 °C. This trend may be related to an increase in molecular weight, stability, and degree of aromatization during the composting process [5].

3.3. Experiment III: evolution of the thermophilic digestion of primary sludge and OFMSW

The substrate used was a mixture of two different types of waste. In the DTG profile (Fig. 6), it is possible to observe the weight loss experienced at low temperature by readily oxidized material both for the primary sludge and for the OFMSW. For the feed sample Feed-PS:OF, the low temperature peak (around 300 °C) has its initial formation at 140 °C. This early presence is due to the substances making up the readily degradable organic matter of primary sludge [6]. As the stages of the stabilization

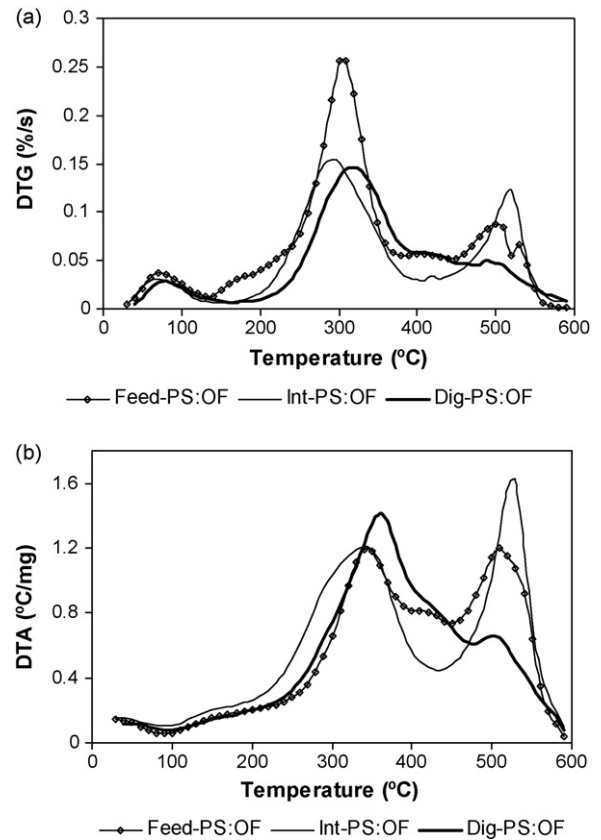


Fig. 6. (a) Evolution of the weight-loss profile in an oxidizing atmosphere (DTG). (b) Changes in DTA signals in an oxidizing atmosphere of the thermophilic digestion system for primary sludge and OFMSW.

process proceed, the intensity of the first peak diminishes, this being reflected not only in the profiles but also in the previous systems studied.

The DTG profile of sample Int-PS:OF shows how the first peak begins at a later point, clearly indicating that the readily oxidized material in the primary sludge has been consumed. The intensity of this peak at low temperature is, of course, lower than that registered for Feed-PS:OF; this is a characteristic of the evolution of the stabilization process. Unlike what happens in the mesophilic digestion systems, the digestate sample Dig-PS:OF from the thermophilic system does not present any major peak at high temperature. Furthermore, although this peak is present at an intermediate stage of the digestion process (see Int-PS:OF DTG profile, Fig. 6a), a noteworthy reduction in its intensity is observed by the end of the stabilization.

The changes in the DTG profiles for this system in the low temperature range (250–400 °C) follow a similar pattern to that observed both in the mesophilic system previously studied in this research and for the wastes studied by Gomez et al. [6]. Once the stabilization process has ended, a single peak at around 350 °C is observed for the digestate sample. However, when DTA profiles are compared, the profile obtained from the digestate sample Dig-PS:OF shows a higher release of energy in the low temperature range than the DTA profiles obtained from the Feed-PS:OF and Int-PS:OF samples. This result runs counter to what occurs with mesophilic systems in the digestion and co-digestion of

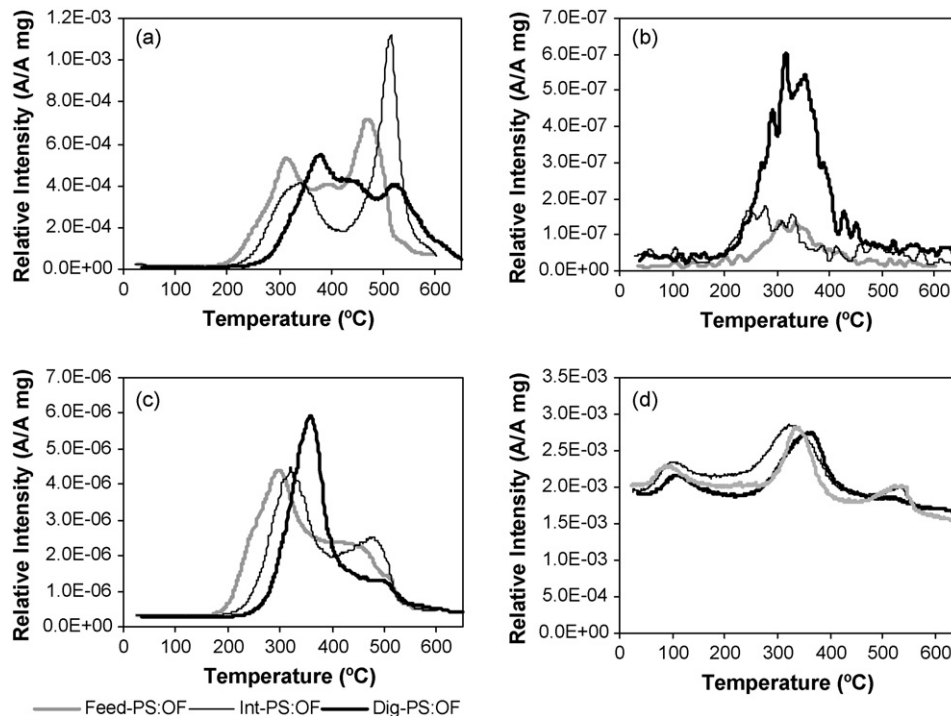


Fig. 7. Evolution of the emission profiles for mass/charge (m/z) signals: (a) 44, (b) 64, (c) 41 and (d) 18, in an oxidizing atmosphere of the thermophilic digestion system for primary sludge and OFMSW.

primary sludge and the OFMSW, where a reduction in energy release in the low temperature range is observed at the end of the stabilization process [6].

In the high temperature region, the evolution of the DTG and DTA profiles differs from the previous cases studied. In the thermophilic processes, the presence of a peak related to loss of weight at 550 °C is observed in the sample corresponding to an intermediate stage. However, as the stabilization process continues, this peak declines considerably in size and is confirmed by the evolution of m/z 44 emission.

Fig. 7 presents the signals recorded for the m/z proportions 44, 64, 41 and 18. As in the cases of digestion already considered, an increase in SO_2 emissions is observed as stabilization progresses (m/z 64, sample Dig-PS:OF). The behaviour of signals m/z 44 and 41 is similar to the evolution of DTA signal, just as in the previous cases. For signal m/z 18 the maxima occur in the low temperature range, the first being related to reductions in humidity and the second to the oxidation of organic compounds rich in hydrogen.

4. Conclusions

In the stabilization processes studied in these experiments and in the authors' previous already published work, thermal methods have proven to be an appropriate tool for assessing the degree of stabilization attained by organic matter under anaerobic digestion. From the results, it was observed that anaerobic stabilization leads to a reduction in the intensity of the peak at low temperatures registered by DTG profiles. The stabilization process evolves so as to generate a single peak around 350 °C. In the high temperature range, the DTG profiles present great

variety, but the presence of a peak around 550 °C is characteristic. However, the thermophilic process is an exception in which this peak decreases in size at the end of stabilization.

The emissions registered by the mass spectrometer help to shed light on the process, although they are not conclusive. From the results obtained, a major release at high temperature for mesophilic systems was observed from the CO_2 ion current, while the thermophilic system showed the opposite behaviour, with its maximum at low temperature. In all cases studied, the signal corresponding to volatile compounds of low molecular weight (m/z 41) presents a tendency to situate the maximum at low temperatures at the end of the digestion process. The main release of water (disregarding the dehydration process) is related to the thermal degradation of easily oxidized compounds.

References

- [1] M.S. Switzerbaum, H.M. Lynne, El Epstein, A.B. Pincince, J.F. Donovan, Defining Biosolids Stability: A Basis for Public and Regulatory Acceptance, Project 94-Rem-1, Water Environment Research Foundation, 1997.
- [2] P. Balmer, B. Kaffehr, Differential thermal analysis for the characterization of the stability of sludge, in: P. L'Hermite, H. Ott (Eds.), Characterization, Treatment and Use of Sewage Sludge, Reidel, Dordrecht, Holland, 1981, pp. 44–54.
- [3] M. Dell'Abate, S. Canali, A. Trincer, A. Benedetti, P. Sequi, Thermal analysis in the evaluation of compost stability: a comparison with humification parameters, *Nutr. Cycl. Agroecosyst.* 51 (1998) 124–217.
- [4] M. Otero, L.F. Calvo, B. Estrada, A.I. García, A. Morán, Thermogravimetry as a technique for establishing the stabilization progress of sludge from waste-water treatment plants, *Thermochim. Acta* 389 (2002) 121–132.
- [5] M. Pietro, C. Paola, Thermal analysis for the evaluation of the organic matter evolution during municipal solid waste aerobic composting process, *Thermochim. Acta* 413 (2004) 209–214.

- [6] X. Gómez, M.J. Cuertos, A.I. García, A. Morán, Evaluation of digestate stability from anaerobic processes by thermogravimetric analysis, *Thermochim. Acta* 426 (2005) 179–184.
- [7] A.J. Higgins, A. Kapplovsky, J. Hunter, Organic composition of aerobic, anaerobic and compost-stabilized sludges, *Water Pollut. Contr. Feder.* 54 (1982) 466–473.
- [8] M.F. Gómez-Rico, R. Font, A. Fullana, I. Martín-Gullón, Thermogravimetric study of different sewage sludges and their relationship with the nitrogen content, *J. Anal. Appl. Pyrol.* 74 (2005) 421–428.
- [9] R. Font, A. Fullana, J.A. Conesa, F. Llavador, Analysis of the pyrolysis and combustion of different sewage sludges by TG, *J. Anal. Appl. Pyrol.* 58–59 (2001) 927–941.
- [10] R. Font, A. Fullana, J. Conesa, Kinetic models for the pyrolysis and combustion of two types of sewage sludge, *J. Anal. Appl. Pyrol.* 74 (2005) 429–438.
- [11] E. Smidt, P. Lechner, Study on the degradation and stabilization of organic matter in waste by means of thermal analyses, *Thermochim. Acta* 438 (2005) 22–28.
- [12] C.P. Marshall, G.S. Kamali Kannangara, M.A. Wilson, J.-P. Guerbois, B. Hartung-Kagi, et al., Potential of thermogravimetric analysis coupled with mass spectrometry for the evolution of kerogen in source rocks, *Chem. Geol.* 184 (2002) 185–194.
- [13] Q. Wang, M. Odlyha, N.S. Cohen, Thermal analyses of selected soil samples from the tombs at the Tianma-Qucun site, Shanxi, China, *Thermochim. Acta* 365 (2000) 189–195.
- [14] M. Dell'Abate, A. Benedetti, A. Trincher, C. Dazzi, Humic substances along the profiles of two typical Haploxerert, *Geoderma* 107 (2002) 281–296.
- [15] M. Dell'Abate, A. Benedetti, P.C. Brookes, Hyphenated techniques of thermal analysis for characterisation of soil humic substances, *J. Separ. Sci.* 26 (2003) 433–440.
- [16] C. Siewert, Rapid screening of soil properties using thermogravimetry, *Soil Sci. Soc. Am. J.* 68 (2004) 1656–1661.
- [17] A.F. Plante, M. Pernes, C. Chenu, Changes in clay-associated organic matter quality in a C depletion sequence as measured by differential thermal analyses, *Geoderma* 129 (2005) 186–199.
- [18] E. Lopez-Capel, S.P. Sohi, J.L. Gaunt, D.A. Manning, Use of thermogravimetry-differential scanning calorimetry to characterize modelable soil organic matter fractions, *Soil Sci. Soc. Am. J.* 69 (2005) 136–140.
- [19] W. Geyer, F.A.-H. Hemidi, L. Brüggemann, G. Hanschmann, Investigation of soil humic substances from different environments using TG-FTIR and multivariate data analysis, *Thermochim. Acta* 361 (2000) 139–146.
- [20] E. Smidt, K.-U. Eckhardt, P. Lechner, H.-R. Schulten, P. Leinweber, Characterization of different decomposition stages of biowaste using FT-IR spectroscopy and pyrolysis-field ionization mass spectrometry, *Biodegradation* 16 (2005) 67–79.
- [21] C. Díez, Valorización energética de neumáticos fuera de uso, Seguimiento cinético del proceso de pirólisis, Tesis doctoral, Departamento de física, química y expresión gráfica, Universidad de León, 2003.
- [22] M.E. Sánchez, Gestión de residuos orgánicos y plásticos, Aprovechamiento energético mediante pirólisis, Departamento de física, química y expresión gráfica, Universidad de León, 2004.
- [23] J. Jauhiainen, J. Conesa, R. Font, I. Martín-Gullón, Kinetics of pyrolysis and combustion of olive oil solid waste, *J. Anal. Appl. Pyrol.* 72 (2004) 9–15.
- [24] R. Radmanesh, Y. Courbariaux, J. Chaouki, C. Guy, A unified lumped approach in kinetic modeling of biomass pyrolysis, *Fuel* 85 (2006) 1211–1220.
- [25] A. Arenillas, F. Rubiera, J.J. Pis, Simultaneous thermogravimetric-mass spectrometric study on the pyrolysis behaviour of different rank coals, *J. Anal. Appl. Pyrol.* 50 (1999) 31–46.
- [26] D.L. Urban, M.J. Antal Jr., Study of the kinetics of sewage sludge pyrolysis using DSC and TGA, *Fuel* 61 (1982) 799–806.
- [27] J.A. Conesa, A. Marcilla, D. Prats, M. Rodríguez, Kinetic study of the pyrolysis of sewage sludge, *Waste Manage. Res.* 15 (1997) 293–305.