Available online at www.sciencedirect.com
SCIENCE DIRECT®

Thermochimica Acta 426 (2005) 179–184

thermochimica acta

www.elsevier.com/locate/tca

Evaluation of digestate stability from anaerobic process by thermogravimetric analysis

X. Gómez, M.J. Cuetos, A.I. García, A. Morán*

Chemical Engineering Department, University of León, IRENA-ESTIA, Avda. de Portugal 41, León 24071, Spain

Received 3 May 2004; accepted 29 July 2004
Available online 28 August 2004

Abstract

A study aimed to monitor the anaerobic digestion process using thermal analysis to define the stability of the digestate obtained was conducted. The mesophilic digestion of primary sludge (PS), of the organic fraction of municipal solid wastes (OFMSW), and of a mixture of these two biowastes was evaluated. Temperature-programmed combustion tests were carried out to investigate the stabilization degree of samples throughout the digestion process. The DTG profile obtained from combustion in an oxidizing atmosphere for the samples analysed showed, as a common result, reduction at low temperatures together with an increase at high temperatures (around 500 °C) of the intensity of the rate of loss of mass as the stabilization process evolved. In all digestate samples the DTA signal showed energy release at high temperatures (around 500 °C) which was not present in feed samples. This study shows that thermogravimetry may offer a means of ascertaining the stabilization degree reached by the organic matter under the anaerobic digestion process.

Keywords: Anaerobic process; Thermogravimetric analysis; Biowastes

1. Introduction

Application to the land of biosolids derived from anaerobic digestion processes (also termed digestate or peat, to highlight its difference from compost obtained through aerobic processes) is the most attractive option in terms of environmental issues. This is because of the recovery of nutrients attained and the attenuation of the loss of organic matter suffered by soils under agricultural exploitation. At the present day, biosolids from wastewater treatment plants (WWTP) are applied under regulations that are becoming more restrictive. In Spain, the relevant regulation is Royal Decree 1310/1990 published in the BOE [State Official Gazette] on 1 November 1990 and for the European Union the regulation is 86/278/CEE of 12 June 1986. A new draft is currently being prepared, which is intended to impose greater restrictions on some toxic substances. In the US, the application of biosolids is covered by EPA 40 CFR-Part 503 Regulations. Up to the present this regulation has proved effective in protecting public health.

The regulations relating to land application of biosolids make imperative a, prior application via biological, chemical or thermal technology, storage for an extended period, or any other procedure capable of significantly reducing the fermentative capacity of biosolids and any risk to health arising from application to the land. Effectively, application of biosolids to the land requires them to be stabilized [1]. The three principal objectives of stabilization are the reduction of pathogens, the elimination of unpleasant smells, and decreasing or eliminating the potential for putrefaction [2]. Nevertheless, assessment of these objectives is not an easy task in respect of sewage sludge. It becomes even more complicated when dealing with the stabilization of any other residue, as for instance the digestate from the organic fraction of municipal solid wastes, owing to the great number of definitions given for the concept of stabilization and the

---

* Corresponding author. Tel.: + 34 987 291841; fax: +34 987 291839.
E-mail address: dfqamp@unileon.es (A. Morán).

0040-6031/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2004.07.019

large number of methods for measuring the degree of stabilization. There is still no simple, reliable and universally acceptable analytical method for assessing the stability of biosolids.

There are as many analytical methods claiming to evaluate the degree of stabilization of biosolids as there are definitions for the concept of stabilization. Determination of the degree of stabilization should be based on several tests giving complementary information [3]. Nevertheless, the lack of any standardization impedes the comparison of results from existing analytical techniques.

On the basis of the loss of energy undergone by materials during biological stabilization, Otero et al. [4] proposed the use of thermal analysis (thermogravimetric analysis (TGA) and differential thermal analysis (DTA)) as a technique for evaluating the degree of stabilization of biosolids. The use of such techniques is justified by the mineralization and conversion of organic matter into humic substances during biological stabilization processes and the reduction in the energy available for the metabolisms of micro-organisms as the stabilization process takes place. Hence, the use of an ignition index gives information relating to the combustible organic fraction and the energy released [5].

Thermogravimetric analysis (TGA) is a technique based on the weight lost by a sample under programmed heating in a controlled atmosphere. The rate of the weight loss undergone by the sample is the basis of differential thermogravimetry (DTG). Differential thermal analysis (DTA) is based on the temperature changes in the sample as compared to an inert sample subjected to the same rate of heating. The DTG profile makes it possible to determine the weight loss that occurs in a given sample at every temperature measured during combustion. Monitoring the biological stabilization processes by TG-DTG would lead to expectations of an increase in the combustion waste of the sample linked to a decrease in the organic fraction of the sludge as the degree of stabilization increases [6].

Otero et al. [4] showed that thermogravimetric analysis can be used in monitoring the stabilization process for waste-activated sludge under aerobic conditions. Pietro and Paola [7] proposed the use of thermal analysis to monitor the composting process in the 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.

The work reported here was intended to study the anaerobic digestion processes for various substrates using thermogravimetric analysis as a monitoring tool. The digestion of primary sludge (PS), of the organic fraction of municipal solid wastes (OFMSW), and of a mixture of these two wastes was evaluated. The digestate obtained from the stabilization process was subjected to program heating under oxidizing conditions, in accordance with the method proposed by Otero et al. for monitoring the aerobic stabilization of sewage sludge [4].

2. Materials and methods

2.1. Experimental procedure

The experimental work was carried out in two stages. During the first stage, three anaerobic digesters were set up. These reactors worked continuously in the mesophilic range (34 °C). The substrates used for digestion were primary sludge (PS), the organic fraction of municipal solid wastes (OFMSW), and a mixture of these residues in a proportion of 50% each.

For the second stage of the experimental work, anaerobic digestion trials under batch conditions were performed. For these trials, the same substrates were used as feed and the digestate obtained from the reactors under continuous operation was used as inoculum. The first part of the experiment provided a sample of digestate at a determined hydraulic retention time (HRT), while the second stage yielded a sample of digestate that had not been submitted to the complete digestion process.

The PS used in this experiment was obtained from the wastewater treatment plant (WWTP) of the city of Leon in Spain, with a capacity of 150,000 PE (population equivalent). Its content of heavy metals and micro-pollutants is in accordance with the limits imposed by the Spanish legislation (R.D. 1310/90) and European directive 86/278/CEE. The PS was concentrated to a total solid content of 6% and stored at 4 °C prior to its use. The OFMSW was simulated by mixing the following components: 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.

2.1.1. Experiment I

During this stage the digesters were in continuous operation. The reactors used were designated in accordance with the substrate being digested, R-PS for the reactor using PS, R-OF for the reactor digesting the OFMSW and R-PS:OF for the digester handling the mixture of wastes. This mixture was such that the PS fraction represented 50% of its total solid content. The reactors had a volume of 3 l, were fed daily and were equipped with a mechanical stirrer. The temperature of the process was maintained at 34 °C using a jacket with thermostat. The HRT of the reactors was 41 days.

2.1.2. Experiment II

This experiment was carried out so as to obtain a sample that had not been subjected to the full digestion process. The digestion was performed under batch conditions for 5 days, using Erlenmeyer flasks of 100 ml working volume. The Erlenmeyer flasks were provided with a magnetic stirrer and immersed in a water bath at 34 °C. This experiment used the digestate obtained from Experiment I as inoculum and the feed appropriate for each case under study. The volumetric proportion inoculum:feed was 5:3.

2.2. Analytic 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. The 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^{-1} to 600 °C with a flow-rate of 100 ml min^{-1} of synthetic air (composition 21 ± 1% O_2 and 79 ± 1% N_2; purity ≥99.9994%). The manometric pressure was maintained at 101 kPa.

3. Results

The digesters were studied for a HRT of 41 days. Table 1 presents the results obtained for the pH values, and the VS and TS content for the samples of feed, for the sample corresponding to an intermediate stage in the digestion process, obtained from the batch trials, and for the sample of digestate obtained from the reactors.

The reduction in volatile solids shown in Table 1 relates to the reduction attained by the anaerobic digesters in continuous operation being the digestate sample obtained from these reactors. The greater reduction in VS achieved by the systems in which the OFMSW was part of the feed is plain. This is due to the greater VS content of this type of waste. For all the systems under study the reduction of volatile solids obtained was greater than 50%.

In the three systems under study an increase in pH values was noted as the digestion process took place. With respect to the gas production of the reactors, R-PS showed an average gas production of 1.1 l day^{-1}, the R-OF reactor had a gas production of 2.0 l day^{-1} and the R-PS:OF reactor digesting the mixture showed a gas production of 1.7 l day^{-1}. These results are in accordance with the values reported in the literature for the organic loading rate applied [8–10].

Table 1
pH, TS and VS content for the samples of feed, digestate from the batch trials (intermediate stage), and digestate from the reactors for the systems under study

Sample		PS	OF	PS:OF
Feed	pH	5.23	3.4	3.6
	[VS] (g l^{-1})	42.8	50.6	52.5
	[TS] (g l^{-1})	61	54.8	64.3
Intermediate stage	pH	7.16	4.49	6.11
	[VS] (g l^{-1})	34.1	19.8	22.6
	[TS] (g l^{-1})	58.1	24.4	34
Digestate	pH	7.4	7.2	7.1
	[VS] (g l^{-1})	19.5	13.5	12.5
	[TS] (g l^{-1})	35.4	24.4	21.4
	VS reduction %	54.4	73.3	76

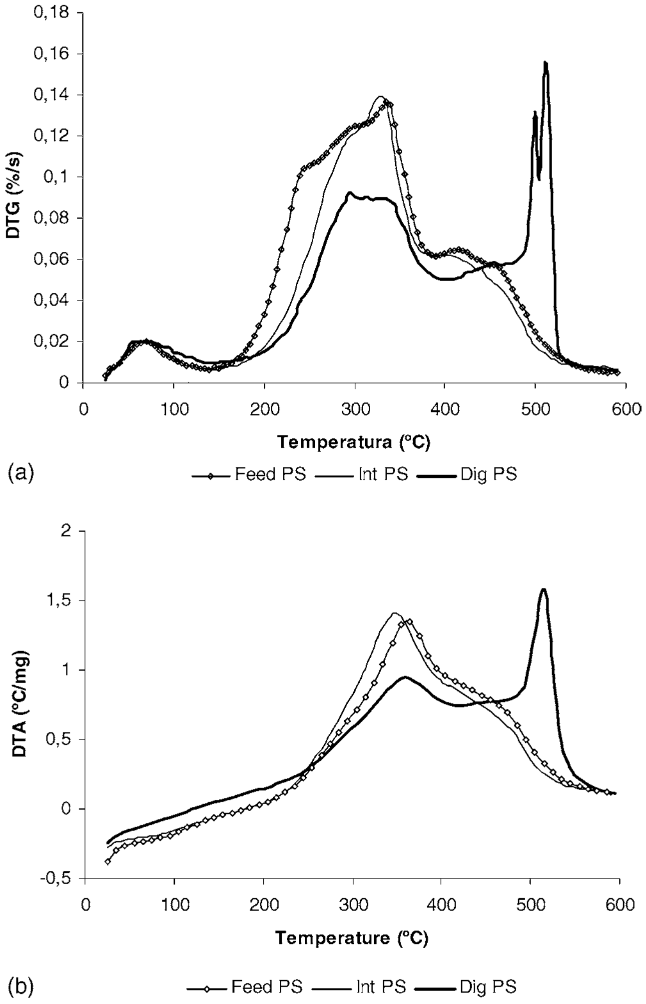

Fig. 1. (a) Evolution of the weight-loss profile in an oxidizing atmosphere (DTG). (b) Evolution of DTA signals in an oxidizing atmosphere for the PS system.

3.1. DTG and DTA profiles for the digestion process of primary sludge (PS)

Fig. 1 presents the results obtained from the thermal analysis performed for samples from the PS system. Fig. 1(a) represents the DTG profile for the feed sample (Feed-PS), the digestate sample from the reactor in continuous operation (Dig-PD), and the sample obtained from the batch trials corresponding to an intermediate stage (Int-PS).

All the DTG profiles show a characteristic peak for readily oxidized material. The intensity of this peak decreases as the stabilization process goes on, indicating that the availability for micro-organisms of material susceptible of conversion is diminishing. This behaviour is also reported by Otero et al. [4] for samples of secondary sludge from various wastewater treatment plants undergoing aerobic stabilization.

The DTG profile of the feed sample (Feed-PS) began with a major peak before the temperature reached 200 °C. As the stabilization process continued, this peak was displaced to higher temperatures, with a decrease in its intensity. Only

Table 2
Residue remaining at 600 °C and temperature by which the material had lost 50% of its original mass (T_{50})

System	Material remaining at 600 °C (%)			T_{50} (°C)		
	Feed	Int	Dig	Feed	Int	Dig
PS	33	42.5	43.6	391	446	505
OF	6.4	7	40	322	334	507
PS:OF	17.8	32.3	35.6	338	384	462

the sample of digestate obtained from the reactor (Dig-PS) showed a peak around 500 °C, the presence of which may be related to organic matter with complex structures, generated by metabolic activity. Once the oxidation process for this material had taken place, weight loss occurred in a narrow range.

Table 2 presents details of the amount of material remaining from the substrates studied once oxidation was completed (expressed as a percentage of the initial mass of the material). The final temperature of the heating process was 600 °C. This table also shows the temperature by which the material had lost half its weight, or to put it in other terms, the temperature at which the material showed a loss of 50% of its original mass (T_{50}). Table 2 shows an increase in the amount of material remaining at 600 °C as the stabilization process took place, along with an increase in T_{50}. These two facts may be of use when the transformations undergone by materials during the anaerobic digestion process are being considered, since the conversions may be reflected in their thermogravimetric behaviour.

Simultaneously to the registration of the mass loss signal, the apparatus also recorded the DTA signal from the primary sludge combustion. The DTA signal showed an exothermic process related to the energy release from combustion. It is important to note the exothermic peak that was related to the loss of mass suffered by Dig-PS at high temperatures. For this sample in particular, the release of energy was lower at low temperatures. This was the opposite of the behaviour of the Feed-PS and Int-PS samples, both of which present a major release of energy at low temperatures.

3.2. DTG and DTA profiles for the digestion process of the organic fraction of municipal solid wastes (OFMSW)

Just as the digestion process for the PS system was followed, the same was done with the OFMSW system. Fig. 2 shows the profiles obtained from thermal analysis. The lines represent the results for the feed sample denoted Feed-OF, for the sample from an intermediate digestion stage described as Int-OF and for the digested sample Dig-OF.

The materials constituting the feed for this system presented two clearly separated zones in the DTG profile, one around 300 °C and the other in the range 450–500 °C. This is in contrast to the profile presented by Feed-PS, in which weight loss was continuous from 200 °C until 500 °C was reached. In addition, the low temperature peak for Feed-OF began at higher temperatures, as compared with the first peak of Feed-PS. In the high temperature range two high-intensity peaks were present, corresponding to structurally complex materials, while the intensity of the peaks for the materials in Feed-PS was lower at the same temperature range.

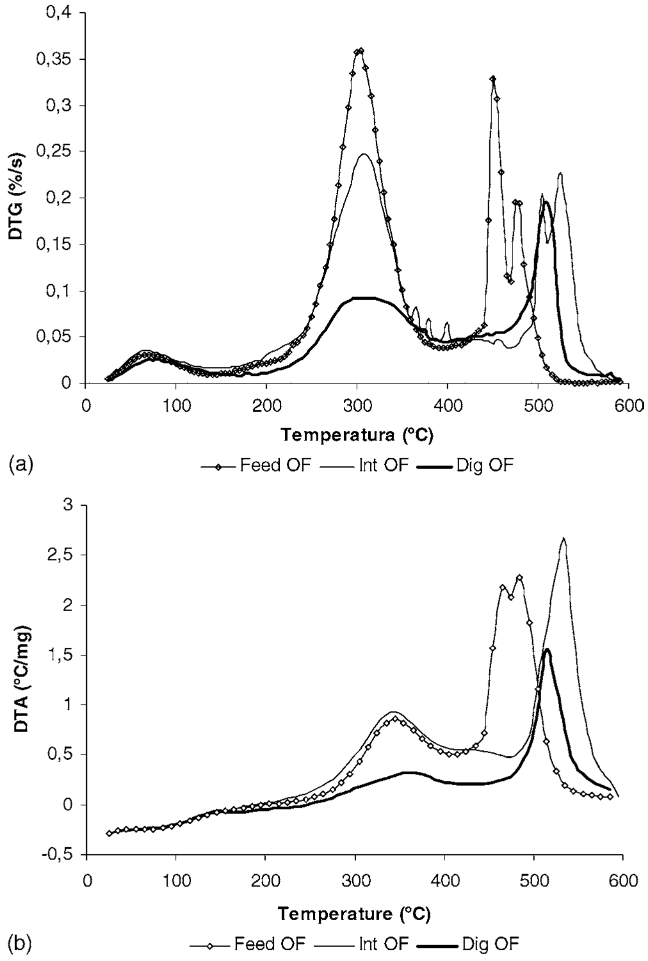

Fig. 2. (a) Evolution of the weight-loss profile in an oxidizing atmosphere (DTG). (b) Evolution of DTA signals in an oxidizing atmosphere for the OFMSW system.

As the digestion process progressed, the intensity of the peak representing materials that oxidize readily decreased, while the two peaks representing complex materials were displaced to higher temperatures (see profile of Int-OF) and the first of these two peaks underwent a decrease in intensity. Once the digestion process had been completed, the Dig-OF sample presented a greater reduction in size for the peak at low temperatures and a single peak at high temperatures. The profile obtained from this sample was similar in behaviour to that obtained from the digestate of the PS system.

Just as for PS, Table 2 also sets out the results for the OFMSW system. Here, too, there was an increase in the residue remaining after the combustion process had been completed together with the growth in T_{50} as the digestion process progressed. It was noteworthy that the Feed-OF sample had lost 50% of its original mass by 322 °C, while

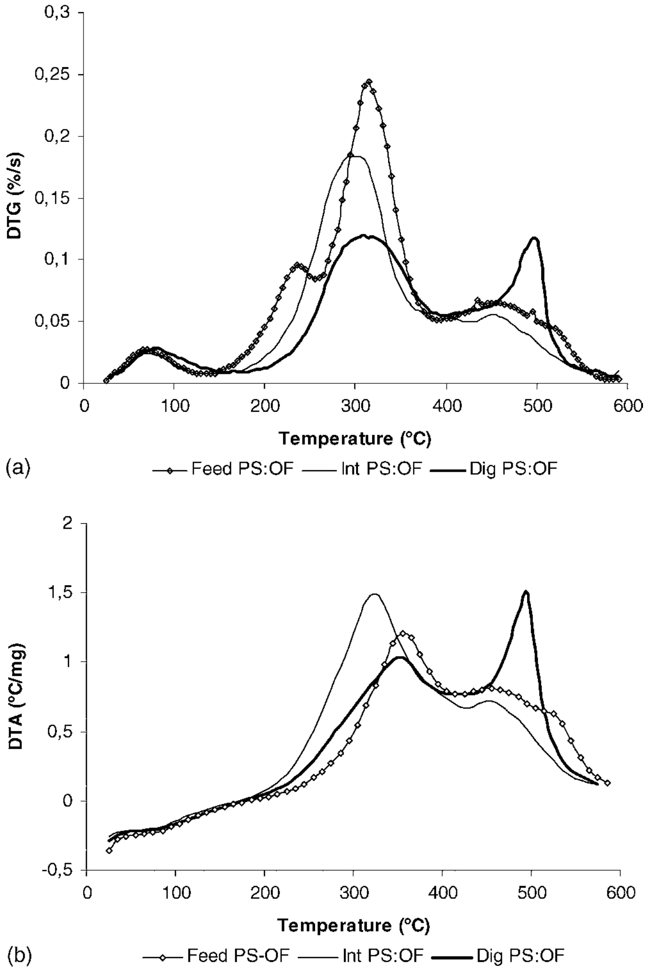

Fig. 3. (a) Evolution of the weight-loss profile in an oxidizing atmosphere (DTG). (b) Evolution of DTA signals in an oxidizing atmosphere for the PS:OFMSW mixture system.

for Feed-PS this happened at 391 °C. This may explain the greater production of gas by the R-OF reactor (2.0 l day^{-1}) as compared with R-PS (1.1 l day^{-1}). Moreover, the amount of residue remaining at 600 °C was greater for Feed-OF than it was for Feed-PS.

The DTA signal presented in Fig. 2(b) shows a higher energy release at the high temperature range for the three samples taken, this being in accordance with the loss of mass experienced at this same temperature range. At low temperatures, even though a noteworthy loss of mass appeared in the DTG profiles, the associated energy release was low. This is characteristic of combustion processes occurring at low temperatures.

3.3. DTG and DTA profiles for the digestion process of the mixture of primary sludge (PS) and the organic fraction of municipal solid wastes (OFMSW)

The DTG and DTA profiles for this system are presented in Fig. 3, with Feed-PS:OF denoting the sample of mixed feed, Int-PS:OF the sample at an intermediate stage in the digestion process, and Dig-PS:OF the digestate sample obtained from the continuous reactor once the stabilization process had been completed.

Feed-PS:OF presented a first peak in the DTG profile at around 200 °C, followed by a second peak at 300 °C (Fig. 3(a)). These two peaks represent materials that are readily oxidized. Since the sample comprises a mixture, the first peak would relate to components of the PS and the second peak to components of the OFMSW.

The profile of the Int-PS:OF sample no longer had a separate peak around 200 °C. On the contrary, it presented a single peak lying in an intermediate temperature range in relation to the two peaks at low temperatures presented by the feed sample. The easily oxidized materials supplied by the PS would be the first to be consumed by micro-organisms, explaining the loss of the peak at 200 °C in the DTG profile.

In the DTG profile of the Dig-PS:OF sample there is a considerable reduction in the size of the peak at low temperature as the stabilization process takes place. However, if a comparison is made with the profiles of the other digestates studied (Dig-PS and Dig-OF) it can be seen that the reduction noted for this peak is the smallest. In addition, the height of the peak at high temperature (around 500 °C) for the Dig-PS:OF sample is the smallest when compared with the other peaks of the digestate samples at this same range of temperatures.

Table 2 also presents the results for the mixture system, with an increase in the amount of residue remaining at 600 °C being evident, as also a growth in T_{50}. It can be also observed that the value of T_{50} for the feed sample of the PS system is greater than the T_{50} value for the mixture system. This could explain the greater gas production of the R-PS:OF reactor (at 1.7 l day^{-1}) as compared with the gas production of R-PS (1.1 l day^{-1}).

As was to be expected, the value of the residue remaining at 600 °C for the feed sample of the mixture system (17.8%) was intermediate between the values obtained for the PS feed sample (33%) and for the OFMSW feed sample (6.4%). The same behaviour was observed in the values for T_{50}. Nevertheless, the behaviour of the Dig-PS:OF digestate obtained from the digestion process differed greatly, having the smallest values for T_{50} and for the residue remaining at 600 °C. It is important to keep in mind that the size of the peak at low temperatures for the Dig-PS:OF sample had the lowest reduction in relation to the other digestates. Consequently, its T_{50} value was the lowest among the three digestates under study.

With respect to the DTA profile presented in Fig. 3(b), a major release of energy can be observed for the Dig-PS:OF sample at high temperatures, just as was the case for the other digestates. The Feed-PS:OF and Int-PS:OF samples presented a considerable release of energy at low temperatures, which was associated with the mass loss experienced by these samples at this same range of temperatures.

4. Conclusions

The anaerobic stabilization processes for different wastes were evaluated using thermal analysis. The DTG profile obtained from combustion in an oxidizing atmosphere for the samples analysed showed, as a common result, reduction at low temperatures together with an increase at high temperatures (around 500 °C) of the intensity of the rate of loss of mass as the stabilization process evolved.

The temperature at which samples lose 50% of their original mass (T_{50}) was found to be greater than 450 °C for digestate samples, while it was below 400 °C for feed samples. In all digestate samples the DTA signal showed energy release at high temperatures (around 500 °C) which was not present in feed samples.

Acknowledgments

This research was made possible through the Project LE 19/04 supported by the Regional Government of Castilla y León (Spain).

References

[1] J.F. Donovan, Developments in wastewater sludge management practices in the United States, in: Proceedings of the Paper Presentation at the New Developments in Wastewater Policy, Management, Technology Conference, Sydney, Australia, 18 May, 1992.
[2] G. Tchobanoglous, F.L. Burton, Ingeniería Sanitaria Tratamiento, evacuación y reutilización de aguas residuales, Metcalf & Hedí Inc., McGraw-Hill/Interamericana de España, SA, 1995.
[3] M.S. Switzesbaum, 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.
[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 wastewater treatment plants, Thermochim. Acta 389 (2002) 121–132.
[5] 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, 1981, pp. 44–54.
[6] A.J. Higgins, A. Kapplovsky, J. Hunter, Organic composition of aerobic, anaerobic and compost stabilized sludges, Water Pollut. Cont. Federation 54 (1982) 466–473.
[7] 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.
[8] G. Bujozek, J.A. Oleskiewicz, S. Danesh, R.R. Sparling, Co-processing of organic fraction of municipal solid waste and primary sludge – stabilization and disinfection, Environ. Technol. 23 (2002) 227–241.
[9] F.J. Callaghan, D.A.J. Wase, K. Thayanity, C.F. Forster, Continuous co-digestion of cattle slurry with fruit and vegetable wastes and chicken manure, Biomass Bioenergy 27 (2002) 71–77.
[10] P.G. Stroot, K.D. McMahon, R.I. Makie, L. Raskin, Anaerobic codigestion of municipal solid waste and biosolids under various mixing conditions – I. Digester performance, Water Res. 35 (7) (2001) 1804–1816.