Thermochimica Acta 528 (2012) 72–75

Contents lists available at SciVerse ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

# Thermal analysis and FTIR studies of sewage sludge produced in treatment plants. The case of sludge in the city of Uberlândia-MG, Brazil

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ARTICLE INFO

*Article history:*
Received 26 August 2011
Received in revised form 4 November 2011
Accepted 8 November 2011
Available online 19 November 2011

*Keywords:*
UASB sludge
Calorific power
Thermal analyses
Pyrolysis
Organic material

ABSTRACT

The operation of anaerobic reactors in Brazil creates a by-product, sewage sludge, for which adequate treatment is necessary to obtain a solid and stable material. The burning of sewage sludge may be an effective alternative for its management, and looking to enhance its energy potential, an environmentally friendly method of disposal is necessary. As the quantity of sludge generated has increased over the past few years, the physical chemical characterization of this waste is the first stage for its utilization as raw material. The material was characterized by thermal analyses (Thermogravimetry (TG)/Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC)) and Infrared Analysis (FTIR) in order to determine the main organic groups present in sludge. The calorific power of the anaerobically digested sludge of Uberlândia-MG, Brazil was measured, and an energy content equal to 16.2 MJ kg$^{-1}$ was found, which is within the range of values reported in the literature.



## 1. Introduction

During the last few years, a veritable revolution of technologies and concepts has emerged concerning domestic wastewater treatment on the world stage [1]. It is within this framework that the growth and development of sewage treatment technologies allowed the applicability of collective anaerobic systems, especially those involved in Anaerobic Sludge Blanket Reactors, known internationally as UASB reactors – Upflow Anaerobic Sludge Blanket reactors [2], which utilization opened new paths in the area of sewage treatment in Brazil, as well as facilitated the expansion and enhancement of the applicability of this process [3].

Because the sludge is a solid by-product with pollutant characteristics, as much at the pathogen level as in the unwanted nutrient content, its final destination is a necessary and complex operation since it involves technical, economic, environmental and legal aspects which usually surpass those of Sewage Treatments Station (STS) [4].

In Uberlândia, a city in the southwest of Brazil, a system of UASB reactors has been adopted, followed by a physical–chemical post treatment, which involves stages of coagulation and flotation. In addition to the UASB sludge generated in the biological stage of treatment, chemical sludge is produced in the physical–chemical treatment system. In each case, it is necessary to discard sludge, i.e., remove it from the liquid phase.

There are several studies involving sewage sludge, as for example: the production of bio-oil from sewage sludge, co-incineration with coal for thermal drying, kinetic modeling of sewage sludge, characterization of pyrolysis products and investigation of its pyrolysis mechanism [5], as well as the application of frying processes for energy recovery in the incineration of sewage sludge [6,7], and the utilization of sludge in the biosorption of heavy metals [8] and in agriculture [9].

Thus, the object of this study was to thermally characterize the UASB sludge, using Differential Scanning Calorimetry (DSC), Thermogravimetry (TG) and Differential Thermal Analysis (DTA), therefore obtaining data regarding the sludge stability by means of the decomposition process, measuring the energetic content of the same sludge generated in the municipal treatment plant using bomb calorimetry, and providing its characterization by FTIR.

## 2. Experimental procedures

Samples of dehydrated sludge originating from the Uberabinha STS and disposed at the landfill in Uberlândia, Minas Gerais, Brazil, have been collected.

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0040-6031/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2011.11.010

The domestic sewage treatment plant is composed of grating and grit chamber (preliminary treatment), upflow anaerobic reactors (UASB), a dissolved air flotation system (coagulation–flotation), centrifuge and geotextile systems, both for dewatering sludge generated in the process, with an estimated monthly production of 264.23 tons of dehydrated sludge, which is consistent with that presented by Aisse et al. [10], which estimates an average production rate of sludge generated in a UASB reactor of 16 g STS hab$^{-1}$ d$^{-1}$.

The collected sample was obtained by dewatering sludge in a centrifuge system (UASB sludge), generating a matrix which was subjected to characterization by thermal analyses (TGA, DTA and DSC), in order to monitor the thermal phenomena of the material and determine its energy potential. This sludge has a solid content of 20%, (13% volatile solids), determined using a drying oven (Nova Ética) model 400/4 ND, muffle furnace (Hydrosan) model HY-200F/DM and an analytical balance (GEHAKA) model AG 200, to carry out the procedures according to the 2540 G method, as described by APHA [11].

Before thermal analyses and FTIR characterization, the sample was sterilized in an a Prismatec CS vertical autoclave at 121 °C for 15 min.

TG and DTA experiments were carried out using a Shimadzu DTG-60 H thermo analyzer from room temperature to 600 °C with a heating rate of 10 °C min$^{-1}$, under a nitrogen flowing rate of 50 mL min$^{-1}$. The sample masses ranged around 5.00 mg.

The superior calorific value (SCV) of the sludge was determined in an IKA C 2000 digital bomb calorimeter, with an IKA KV 600 water refrigeration system. The bomb calorimeter was calibrated with benzoic acid (thermochemical standard) with an average mass of 1.0300 g. The solid sludge sample was compressed into a tablet, yielding an average mass of 1.0438 g. As for the standard, the sample to be analyzed was weighed using a Shimadzu AW 220 balance. A crucible containing the sample was placed in the calorimetric reactor, which worked in the isoperibolic mode at 25 °C. The system was pressurized at 30 bar with oxygen (99.95%) and refrigerated in a thermostatic bath at 20 °C. The measurements, which were duplicated, and calculations of the SCV are compliant with the standards DIN 51900, ISO 1928, ASTM D240, ASTM D1989 and ASTM E711.

The second scan of the DSC thermogram was obtained in a TA DSC Q-20 differential scanning calorimeter. Before the second scan, the material was heated to 200 °C to eliminate any water present in the material, and afterwards the sample was heated in an aluminum crucible at 10 °C min$^{-1}$ from 25 to 500 °C under a nitrogen flowing rate of 50 mL min$^{-1}$.

For FTIR analysis, a tablet was made with 1% (w/w) of the sample dispersed in KBr. The spectra were obtained using a Shimadzu IR Prestige-21 spectrometer. Thirty-two scans were performed with a resolution of 4 cm$^{-1}$.

## 3. Results and discussion

### 3.1. Thermal analysis

TGA and DTA thermograms for the UASB sludge are shown in Fig. 1.

In the TG–DTA curves, three distinct regions are identified. As the sludge sample was not initially dry, there was a mass loss of 72% on the TG curve with a corresponding endotherm around 70 °C, which is due to the release of water from the material, on the DTA curve.

According to Francioso et al. [12], the thermal decomposition of thermolabile components of organic material (proteins and carboxyl groups) produces very significant exothermic reactions at approximately 300 °C, while exothermic reactions at higher temperatures (~450 °C) originate from the decomposition of carbon refractories, such as aromatic rings, N-alkyl long chain structures and saturated aliphatic chains. Unlike the methanogenic sludge DTA curve studied by that author, the UASB sludge DTA curve of our study presented an exothermic reaction accentuated at 453 °C with a mass loss of 10%, and an exothermic reaction less accentuated at 302 °C, losing about 11% of mass. These two exothermic peaks on the DTA curve of the UASB sludge sample shown in Fig. 1 differed from the experimental data presented at the literature [12] because the digestion and settling of the UASB sludge take place in a single reactor with the acetogenic and methanogenic phases and not with the two phases separated, as occurred in the thermal characterization presented by the cited authors.

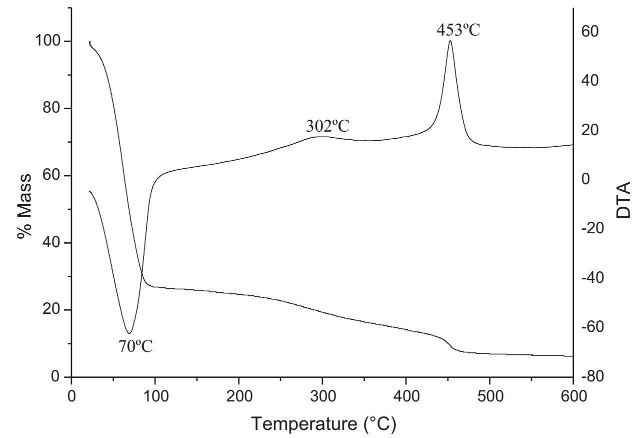


**Fig. 1.** TG–DTA curves of dewatered sludge (UASB sludge).

For UASB sludge, SCV determined by the bomb calorimeter was 16.2 MJ kg$^{-1}$, on a dry basis. After the combustion of the material, a reddish residue was observed in the reactor that contained the sample, probably a result of the mineral material contained in the sludge. This SCV value is 24% higher than the reported by Andreoli et al. [4], who obtained an energy content between 6 and 13 MJ kg$^{-1}$ for digested sludge produced in an anaerobic digester used for the treatment of sludge with high content of unstable organic material. Differences were expected since the data are related to sludge from anaerobic reactors, intended only for stabilization of the solid waste and not generating it inside, all of which occurs in the UASB reactors.

According to Dweck et al., SCV for sludge ranging from 9.50 to 18.57 MJ kg$^{-1}$ have been related, even though the calorific power depends on the specific origin and composition of the sludge [5]. Therefore, 16.2 MJ kg$^{-1}$ on dry basis obtained in the present work confirms that the sludge of Uberlândia's treatment stations is among those with higher calorific power.

Fig. 2 shows the curve obtained from the DSC, second scan, of the UASB sludge, where it is observed the decomposition process, with its respective enthalpies.

As shown in Fig. 2, a first event with an exothermic $\Delta H$ of 4.59 J g$^{-1}$ and a transition temperature of 291 °C, followed by second exothermic event ($\Delta H$ = 11.02 J g$^{-1}$) with a peak temperature at 413 °C. The absence of a thermal event on the DSC curve with endothermic characteristic close to 100 °C indicates that there was not a loss of humidity in the sample, due to the pre-heating stage of the sample in the DSC equipment. These results corroborate those of TG/DTA and show that the enthalpy value related to the second exothermic event is 2.4 times higher than that of the first exothermic event. This result is characteristic of the material produced by the UASB treatment.