CHARACTERIZATION OF RESIDUES (SLUDGE) AEROBIC AND ANAEROBIC ORIGINATING FROM SUGARCANE INDUSTRY OF THE NORTHWEST OF SÃO PAULO (BRAZIL)

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Resumo
O presente artigo descreve o estudo de resíduos de cana-de-açúcar, que consistem em um lodo industrial com potencial impacto negativo sobre o crescimento de plantas. Assim, foi realizada a caracterização dos lodos anaeróbio e aeróbio gerados, obtidos, respectivamente, dos reatores de Lodo Anaeróbio de Fluxo Ascendente (UASB) e de Circulação Interna (IC). Os lodos aeróbio e anaeróbio foram coletados e caracterizados por espectroscopia no infravermelho por transformada de Fourier (FTIR), espectroscopia de absorção atômica em chama (AAS), e sua avaliação pirolítica foi conduzida por meio de curvas termogravimétricas. A matéria orgânica foi decomposta na faixa de temperatura entre 160 °C e 700 °C. As substâncias orgânicas presentes nos lodos foram avaliadas por análise de FTIR, a qual indicou a presença de grupos carboxilatos e outros grupos orgânicos derivados de celulose, lignina e precursores de substâncias húmicas. Os pLarâmetros cinéticos das etapas de desidratação e decomposição térmica foram determinados. Os resultados mostram que diferentes energias de ativação foram obtidas para o processo de decomposição térmica. A análise por FTIR forneceu informações importantes sobre os tipos de matéria orgânica presentes nas amostras de lodo. A análise TG/DTG da pirólise, juntamente com os parâmetros cinéticos, permitiu distinguir as principais etapas que podem ser consideradas em uma reação. A energia de ativação para a etapa de desidratação apresentou comportamento semelhante, enquanto a primeira etapa de decomposição térmica indicou diferenças significativas. A análise por AAS revelou a presença dos íons metálicos Zn, Pb, Fe e Mn em ambas as amostras.
Palavras-chave: lodo; comportamento térmico; absorção atômica; infravermelho.

Abstract
The present paper describes the study of sugarcane residues, which is an industrial sludge which may have a negative impact on plant growth. Thus the characterization of the generated anaerobic and aerobic sludge obtained of Upflow Anaerobic Sludge (UASB) and Internal Circulation (IC) reactors, respectively, were carried out. Aerobic and anaerobic sludges were colleted and both were characterized by FTIR, flame atomic-absorption spectroscopy (AAS) and the pyrolysis evaluation was carried out by thermogravimetric curves. Organic matter was decomposed in the temperature range of 160 and 700 C. Organic substances present in the sludge were evaluate by FTIR analysis, which indicate the presence of carboxylate and other organic groups originated from cellulose, lignin and humic substances precursors. Kinetic parameters of the dehydration and thermal decomposition were valuated. The results show that different activation energies were obtained for thermal decomposition. The FTIR provide important information concerning the organic matter types present in the sludge samples. TG/DTG analysis about the pyrolysis and also the kinetic parameters allows distinguish the

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main stages that can be considered in a reaction. The activation energy for dehydration stage have the same feature, while the first thermal decomposition stage indicates different behaviors. The AAS revealed that Zn, Pb, Fe and Mn metals ions were detected at two samples.
Keywords: sludge; thermal behavior; atomic; absorption.

1 INTRODUCTION

In sugarcane industry, the effluents can be treated from anaerobic reactor (Upflow Anaerobic Sludge Blanket - UASB) (Verstraete, *et al.,* 1996). The UASB system works to digest the sludge by anaerobic bacteria which have a high biomass density, which degrade the organic matter and convert into biogas. Due to improvements for the UASB system, a new series of reactors called Granular Expanded Sludge Bed (EGSB) were developed, The EGSB is a reactor of circulation interns (IC), which allows an effective dilution of mixture of the effluents that enters in the reactor. In other words, in this system occurs a better conditioning for the organic matter to be processed (Lier *et al,.* 1997).

In the Brazil, the sugarcane industries have a great importance because it is an employment source and surrender for many family. However, this industrial sector is also pollutant and due to the implication of the residue on the environment and, consequently, to human life quality, to perform of an accurate investigation about the present components of such generated sludge become necessary (Lopes *et al.,* 2005). Actually, the main disposal processes for sludge include agriculture application, landfilling, and thermal conversion (combustion/incineration). In Brazil, the sludge normally is applied to arable land to improve soil fertility because this practice is inexpensive and easy to operate. Besides, the use of sludge as a nutrient source for agriculture may seems a simple and advantageous alternative, but this disposal routes it has been suppressed due the regulatory agencies (Lopes *et al.,* 2005; Sparks *et al.,* 2003; Maria *et al.,* 2010). Furthermore, the increasing amount of heavy metal in soil is a consequence of technological and industrial processes which can lead to the accumulation of metal ion-contaminant (Silveira *et al.,* 2003; Meunier *et al.,* 2006; Martensson *et al.,* 2005). Thus, the study and metal characterization of sludge as a fertilizer to soil is necessary because the presence of heavy metals ions (e.g. Pb(II), Cd(II)) may occur in sludge and therefore, can affect the soils and limit the use of these materials as fertilizers (Taty-Costodes *et al.,* 2003; Pinamonti *et al.,* 1997; Planquart *et al.* 1999; Zheng *et al.,* 2007). Pantano *et al.* (2014) has been studied the occurrence of Cu and Cr in rivers in the northwestern region of the State of São Paulo, Brazil, where the efficiency of the sedimentary humic substances was evaluated. The authors indicate that the sedimentary humic has a complexation capacity because the high concentration of Cr decrease in water.

Klučáková and Nováčková (2014) use the thermal analysis to study the stability of Cu–humic complexes prepared under several concentrations, with the aim of making the investigation between the bond strength of metal and the ions in the humic complexes. The thermogravimetric results indicate a pattern with the Cu-humic complex, which result in several behaviors. These authors also indicate that the thermal analysis can be used in many researches, as versatile analytical method for the characterization of several compounds from various sources.

Nevertheless, sludge is a heterogeneous compound, which has a wide variety of organic and inorganic components. So, the thermal study of sludge and solid waste has been widely used by different authors. Deng *et al.* (2011), study the moisture of of three typical sludges, according indicated by authors: i) municipal sewage sludge (MSS), ii) printing and dyeing sludge (PDS) and iii) paper mill sludge (PMS). These materials were evaluated by TG-DSC and TG-DTA. Gildemeister *et al*. (2015) has used differential scanning calorimetry (DSC) to assess the water connection in a supramolecular structure involving organic extract dissolved with three different metallic ions. They indicated that the thermal behavior combined with NMR implies in intermolecular cross-link. Schaumann and Mouvenchery (2012) in order evaluate the thermal behavior of soils, indicate the efficiency of the thermal analysis methods in various fields of environmental research. These authors show the use of the nanothermal conditions to study heterogeneous samples as soils and organic matter. Capana *et al.* (2009) relate the thermal characterization of sludge compounds, from water and sewage treatment. In this work, the authors carried out the thermal characterization, infrared spectroscopy (FTIR) and atomic absorption spectroscopy (AAS) investigation of this compound. For TG/DTG analysis the behavior was evaluated to verify the dehydration and thermal decomposition courses, add to the knowledge organic matter present in this compound.

The evaluation of thermal behavior by thermogravimetry (TG/DTG), specially the study of pyrolysis process, can be an alternative to converts organic materials at elevated temperatures of sludge. Therefore, the thermogravimetry (TG) and the kinetic study of parameters obtained of the evaluation of thermal degradation stages can be used to evaluation of the pyrolysis behavior of sludge and also of many others materials.

Thus, the aim of the present study describes the chemical characterization of the generated anaerobic and aerobic sludge obtained of Upflow Anaerobic Sludge (UASB) and Internal Circulation (IC) reactors, respectively. The solids sludges were analyzed by infrared spectroscopy technique (FTIR) and also these compounds were characterized by flame atomic absorption spectrometer (AAS). The pyrolysis was carried out in a thermogravimetric (TG) reaction at three several heating rates in a carbonic atmosphere. In addition, TG curves were also used to obtain the kinetic information about the dehydration and first stage of thermal decomposition.

2 EXPERIMENTAL

Samples of sludge from Upflow Anaerobic Sludge (UASB) and Internal Circulation (IC) reactors, were collected under the guidance of officials from the treatment plant effluent in the industry, localized in region of São José do Rio Preto, São Paulo, State. The samples undergone a process of autoclaving for 1 hour at a temperature of 120 °C to avoid the risk of contamination.

The samples were transported to the laboratory to be mixed and dried in an oven with air circulation at 60°C for 48 hours and stored in a desiccator over anhydrous calcium chloride constant mass. After drying the samples were crushed in a mortar and sieved in a metallic sieve (250 size mesh), thus obtaining the work samples.

TG-DTG curves were obtained from a SDT 2960 (TA Instruments). The curves were obtained using sample sizes around 10 mg in an α-alumina crucible and heating rates of 5, 10 and 20ºC min^{-1} under carbonic gas atmosphere (100 mL min^{-1}). Kinetic evaluations of the stages of dehydration and of the first thermal decomposition were obtained using the obtained data of TG curves from 30 to 400ºC.

For the atomic absorption spectrometry evaluation, the solid samples were digested using nitric acid and hydrogen peroxide. A sample mass of around 2 g of the sample were transferred to a 250 mL tall-form beaker, with a 50 mL of concentrated HNO_3. After a 30 min rest, 5 mL of 30% H_2O_2 was added. The mixture was heat to ebullition and adding more 5 mL of 30% H_2O_2 in every 30 min up to obtain a clean sample. After cooling, the samples were filtrated and transferred to a 100 mL volumetric balloon and completed with water.

The metal ions analysis was carried out in flame atomic-absorption spectroscopy (AAS) (SpectrAAA 50B, Varian Scientific Instruments, using butane/oxygen mixture. The certified reference material (MRC), ions samples solutions, were diluted and measured at the selected atomic lines for each metal ion of interest. All the measurements were carried out in triplicate with flow rate of 2.0 ml min^{-1} and the calibration curves were carried out using MRC diluted solutions of metal ions.

The FTIR was utilized to verity the main organics substances components of the sludge samples. The analysis was carried out using a Nicolet model Impact 400 FT-IR instrument in the 4000–400 cm^{-1} range. The solid samples were pressed to KBr pellets.

2.1 Kinetic Methodology

The kinetic evaluation was carried out by isoconversional method, because of it is a way of obtaining reliable and consistent information and also because it avoids the use of explicit kinetic models (Lourenço *et al.* 2011). Thus, in this work, the kinetic parameters were obtained using the approximation to the integral temperature based on the Jacobi fraction, as proposed by Capela, Capela and Ribeiro (2009).

Kinetic analysis under non-isothermal conditions is usual to consider the integral kinetic equation, defined by

$$\beta = \frac{AE}{Rg(\alpha)} \int_{E/RT}^{\infty} \frac{\exp(-z)}{z^2} dz, \tag{1}$$

where $\beta = dT/dt$ is a constant heating rate (*T* is the temperature and *t* is the time), $g(\alpha)$ is the integral form of the reaction model as a function of the extent of reaction α , *A* is the pre-exponential factor, *E* is the activation energy and *R* is the gas constant.

Kinetic parameters are obtained by fitting equation (1) to experimental data and as consequence, an evaluation of the integral on the right side of the equation (1) is required and is known as the temperature integral. Thus, to approximate the temperature integral for some function that yields suitable estimates to these kinetic parameters. This approximation is a rational function, given by the following equation:

$$\int_{x}^{\infty} \frac{\exp(-z)}{z^2} dz = \frac{\exp(-x)}{x} \frac{x^3 + 14x^2 + 46x + 24}{x^4 + 16x^3 + 72x^2 + 96x + 24} \tag{2}$$

A characteristic experimental curve presents the conversional fraction, α, as a function of the temperature for a given heating rate, β. For each fixed value of α there are corresponding values T_α for temperature, values E_α for activation energy and values A_α for pre-exponential factor.

Replacing the integral in equation (1) by the approximation given in equation (2) is obtained the following expression for heating rate β as a function of $x_\alpha = 10^3 / RT_\alpha$

$$\beta = \frac{\exp(B_\alpha - E_\alpha z_\alpha)}{x_\alpha} \frac{E_\alpha^3 z_\alpha^3 + 14E_\alpha^2 z_\alpha^2 + 46E_\alpha z_\alpha + 24}{E_\alpha^4 z_\alpha^4 + 16E_\alpha^3 z_\alpha^3 + 72E_\alpha^2 z_\alpha^2 + 96E_\alpha z_\alpha + 24}, \tag{3}$$

where the activation energy is in kJ/mol and the parameter B_α is defined as:

$$B_\alpha = \ln\left(\frac{10^3 A_\alpha}{Rg(\alpha)}\right) \tag{4}$$

The estimates of the E_α and B_α can be obtained by the non-linear fitting of the equation (3) to the β values as a function of x_α.

Once the $g(\alpha)$ function has been determined for each conversional fraction of α, the estimation of the Arrhenius pre-exponential factor can be obtained from equation 4 and it is given by the following equation:

$$\hat{A}_\alpha = \frac{R}{10^3}\exp(\hat{B}_\alpha)g(\alpha) \quad (5).$$

3 RESULTS AND DISCUSSION

Infrared spectroscopic data on these samples are shown in Table 1.

Table 1 - Characteristics absorptions bands observed to the organic matter (cellulose, lignin and humic substances precursors) present in the sludge after aerobic and anaerobic decomposition processes.

Compounds	**C = O**	**–COO⁻ υassim.**	**–COO⁻ υsim.**	**O–CH₃ δass.**	**O–CH₃ δsim.**	**C – H**	**C – H (ring)**	**OH**
Aeróbic	1751	1625 – 1589	1380	1485	1467	2850-2920	1250	3470-3400
Anaeróbic	1690	1641 – 1568	1390	1487	1465	2928-2958	1250	3470-3400

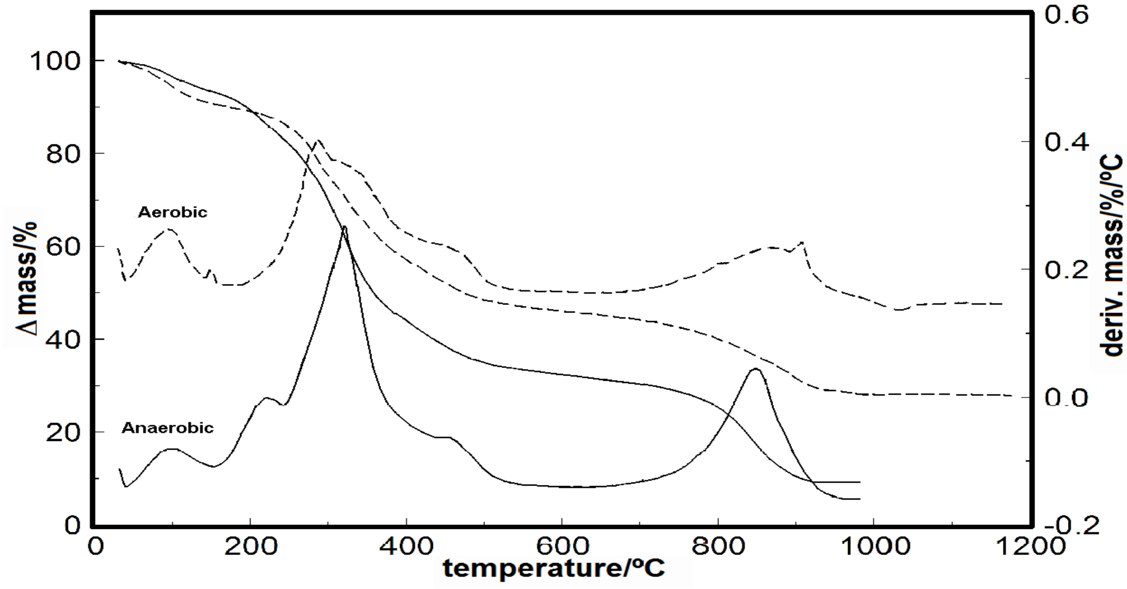
Source: Elaborated by the authors (2026)

The absorptions bands concerning the O–H stretchings might be given to the hydration water and C–O of carbonates, C–H of methyl present in the organic matter (cellulose, lignin and humic substances precursors) (Capana *et al.,* 2009; Nakamoto 1997; Shao *et al.,* 2008).

The obtained values show that aerobic sludge has a metal ions concentration larger than that observed to the anaerobic one. This fact was attributed to the better condition of retention of metal ions, because during the aerobic digestion process the effluent stays more time with the mud (between 5 - 7 days) and therefore, will occurs an increase of the metals presents.

TG/DTG curves provide knowledge of pyrolysis behavior of aerobic and anaerobic sludges under the inert atmosphere. The TG/DTG evaluations are shown in Figure 1, where the mass loss and the rate of mass loss during pyrolysis of the two sludges samples are presented.

Figure 1 - TG/DTG curves of the aerobic sludge (short dash curve), with mass of 9.795 mg, and anaerobic sludge (solid curve), with mass of 9.872 mg, both obtained in carbonic gas atmosphere; heating rate of 20ºC min^{-1}; α-alumina crucible.



Source: Elaborated by the authors (2026).

It was found that the dehydration processes of anaerobic sample occur in the temperature range from 30 to 150 °C with 6.65% of loss, and that the first thermal decomposition stage happened between 150 and 245 °C, with 10.32% of loss, both according DTG curve. According to Shao *et al.* (2008), the first reaction stage is likely attributed to depolymerization reaction of the organic material, while the second stage, that was observed between 245 and 425ºC, with loss of 42%, which it is related to further degradation. The third stage occurs between 425 – 600ºC and to complete the thermal decomposition, the fourth stage occurs between 600 – 950ºC, where the mass losses are 8.69% and 24%, respectively. The temperature ranges for aerobic sample are different from those obtained for anaerobic sample (Figure 1). The dehydration and first thermal decomposition occurred at 30 – 167ºC and 167 – 417ºC, respectively, according to DTG curves, which are attributed to the heterogeneity of the sludge samples. Furthermore, it is possible to see that the first stage of anaerobic sample have two reactions in two well-defined intervals and the sum of mass loss is 52.32%, whereas for the sample aerobic sample the results are overlapping reactions with sum of mass loss of 34.5%. These differences were attributed to the abundant release of volatile matter in anaerobic sample. The third mass loss after the main decomposition or pyrolysis stage started at 417ºC and ends at 670ºC, with loss of 10.65%. As was seen also for the anaerobic sample, the latest thermal decomposition stage occurs between 670 and 985ºC, with mass loss of 16.45%. The remaining masses for anaerobic and aerobic pyrolysis were 8.43% and 28.27 wt %, which demonstrate that, besides of characteristics of pyrolysis the anaerobic an aerobic compounds, these contain more inorganic matter, which also are due to the different sources of the two samples and, therefore are attributed to the their characteristics chemical and physical. In previous paper, Lourenço *et al.* (2011) report by X-ray analysis that these samples have the presence of inorganic compounds as tricalcium aluminate ($Ca_3Al_2O_3$), quartz (SiO_2) and hematite (Fe_2O_3). Thus, these facts suggest that other metal oxides can be presents (which were not detected by X-ray analysis) and therefore, can cause interference in the atomic absorption analysis. The Table 2 shows the results of the analysis carried out by atomic absorption spectra (AAS), where is shown the nature of the inorganic compounds evaluated in this work.

Table 2 - Concentration (mg/kg) of the different metals ions present in aerobic and anaerobic sludge samples.

	Ions						
samples	Zn(II)	Pb(II)	Ni(II)	Fe(III)	Mn(II)	Cu(II)	Cr(III)
anaeróbic	8,9	0,04	_	650	9,0	_	-
aeróbic	12,8	0,08	_	759,5	22,0	_	-
1CETESB*	60	17	13	-	-	35	40
2EMBRAPA*	1500	500	100	-	-	500	300

Source: Elaborated by the authors (2026).

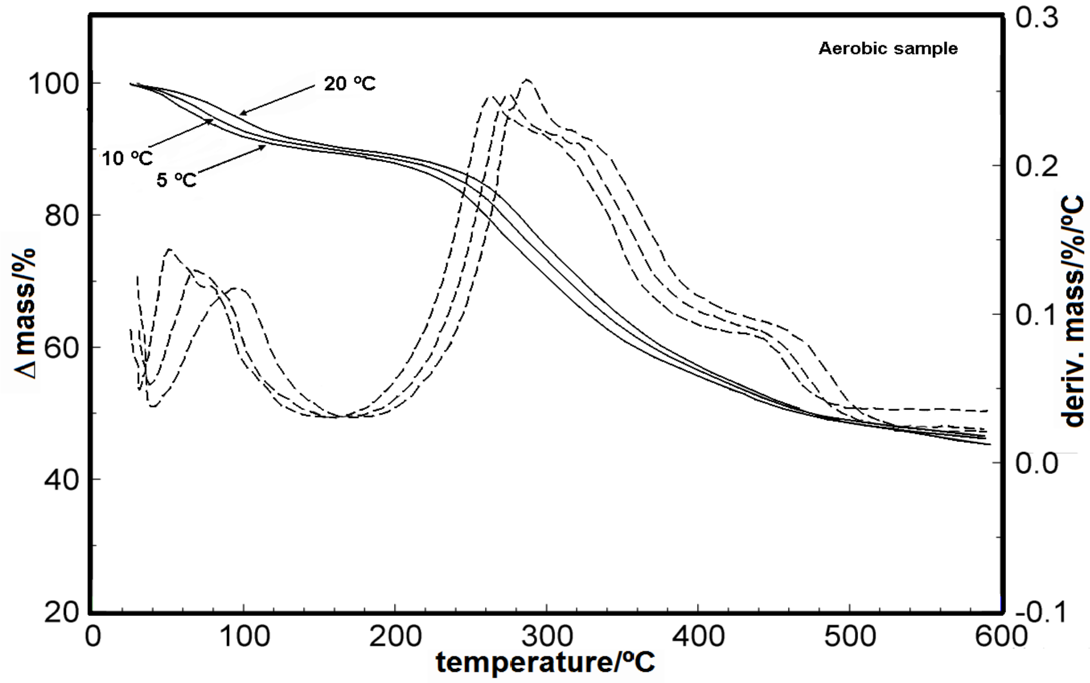
[1]CETESB: minimum permitted in soil and water; [2]EMBRAPA: minimum permitted in soil;
Cobalt ion < limit detection (LD).

The concentrations of metal ions in the samples are expressed by mg/kg, and the others results are standard values permitted in water and soil, which are recommended by Ambient Sanitation Technology Company – CETESB and Brazilian Agricultural Research – EMBRAPA (CETESB 2001; EMBRAPA 1997).

The Figure 2 and 3 showed the TG curves of these samples with heating rates of 5, 10 and 20ºC, but with thermal heating up to 600ºC, because the kinetic study is usually performed only for dehydration and the first stage of thermal decomposition.

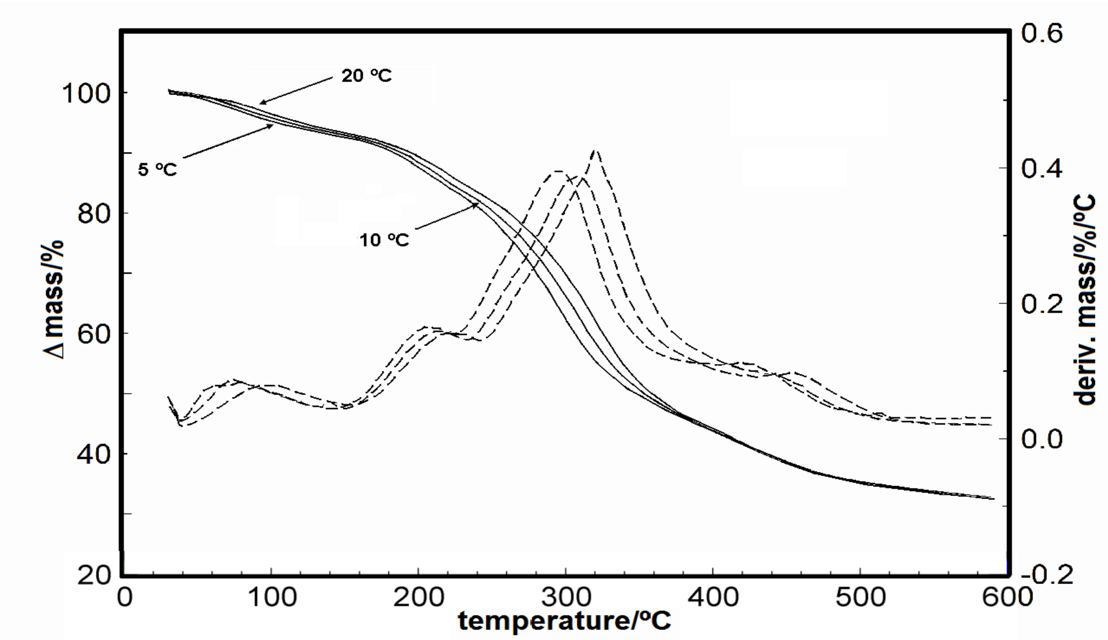
In these TG/DTG curves also it is possible to observer that the heating rate indicate the influence of thermal degradation of the samples. Indeed, there will be a change in mass loss, which is attributed to inertial effect caused by heating velocity (effect of heat transfer on the samples studied). Besides, the use of three heating rates allows lead to obtain data of the kinetic informations during thermal reactions.

Figure 2 - TG/DTG curves of the aerobic sludge, with mass of 9.875 mg, obtained in carbonic gas atmosphere; heating rate of: 5, 10 and 20ºC min^{-1}; aluminum crucible.



Source: Elaborated by the authors (2026).

Figure 3 - TG/DTG curves of the anaerobic sludge, with mass of 9.889 mg obtained in carbonic gas atmosphere; heating rate of: 5, 10 and 20ºC min^{-1}; aluminum crucible.



Source: Elaborated by the authors (2026).

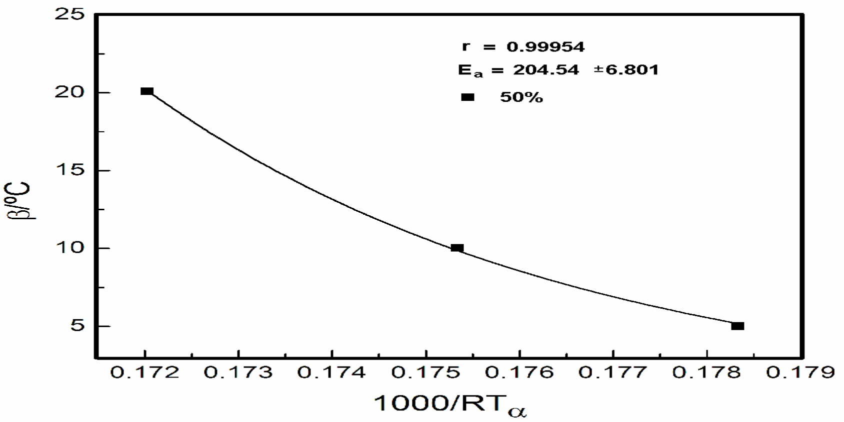
Many researchers have used the kinetic study to determine the reaction behavior during dehydration and thermal decomposition also to improve the perception of reaction (Gašparovič *et al*., 2011; Zhang *et al.* 2014; Yang; Jiang 2009). Shao *et.al.* (2008) indicate the kinetic use for evaluation of several sludges to improve reaction knowledge, while Gašparovič *et al.* (2011)

made the evaluation of the kinetic study of waste water, which indicates the importance of kinetic evaluation on the catalytic pyrolysis attribute to the energy demand of the thermal reactions. As showed for aerobic sample between 30 and 160ºC in the heating rate of 5ºC, this sample has a dehydration process different from the others two rates, where it is possible to see in DTG curve that there are the formation of three shoulders that are attributed to different water losses. For heating of 10°C it is possible to see that occur overlapping reactions, as observed although a slight shoulder peak, while for heating of 20ºC there is only one dehydration stage. The dehydration stage of mass loss of anaerobic sample was not similar to that the behavior observed in aerobic sample. For 5ºC there is the formation of one only shoulder peak, but the continuity of dehydration probably occurs with overlapping reactions without a specific stage. Now, it is possible to see that there are similar thermal decomposition to the both samples, which indicate a single process of behavior thermal.

The kinetic evaluation (activation energy) was calculated, based on the aforementioned principles. Thus, the dehydration and thermal decomposition of the both samples, were evaluated from TG curves (Figures 2 and 3, respectively). As the sludge pyrolysis is very complex, the better option of thermal analysis was the use of mass of 10 mg to obtain the kinetic data, because the use of high sample masses are inadequate due the great number of simultaneous reactions that occur during thermal decomposition.

In the Figure 4 we can see the distribution of the heating rate (β) in function of the $1000/RT_{\alpha}$, which allows to observe the adjustment of activation energy (E_a) for each fixed value of degree conversion (α).

Figure 4 - Diagram of dispersion of β versus degree conversion (α - 50%) of the anaerobic sludge compound in the decomposition stage, with an adjustment for functions.



Source: Elaborated by the authors (2026).

The average values of the activation energy (Ea) of the kinetics data of the different experimental conditions are shown in Table 3.

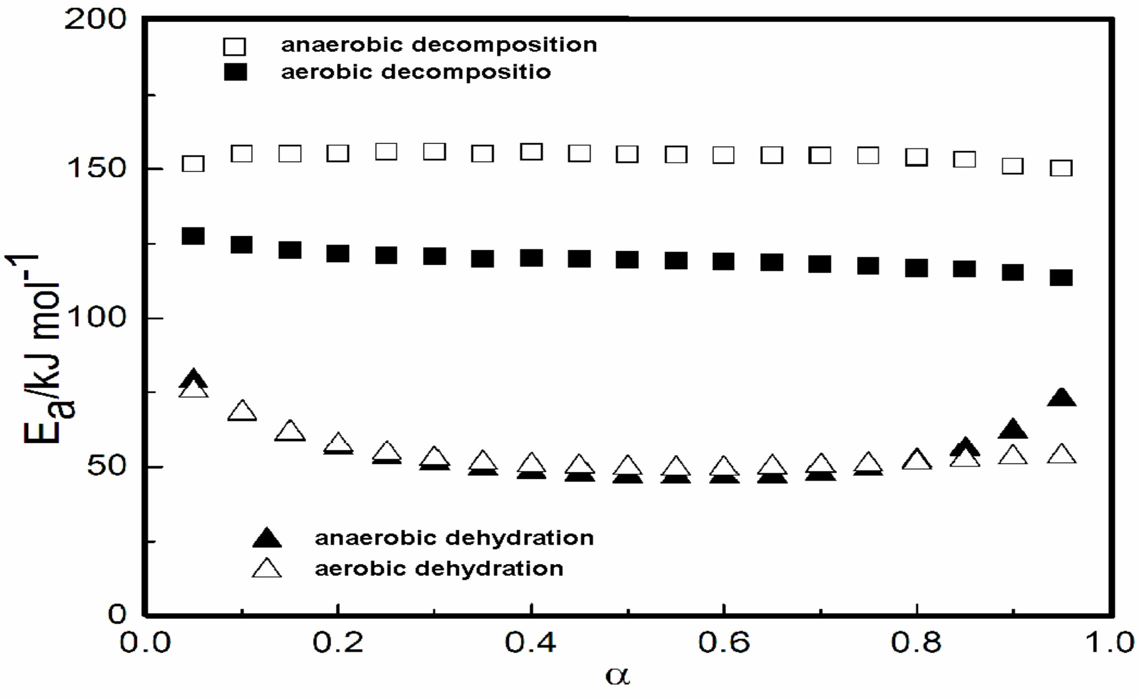
Table 3 - E_a *(kJ mol^{-1})* and correlation coefficient (r) for the stages of dehydration and thermal decomposition.

Compound	*Mass*	**Ea (kJ mol^{-1})*	**r*
Aerobic sludge	dehydration stage	54.86 ± 0.17	0.97819
	1st decomposition stage	119.63 ± 0.03	0.99989
Anaerobic sludge	dehydration stage	55.06 ± 0.14	0.98816
	1st decomposition stage	164.73 ± 0.09	0.99547

Source: Elaborated by the authors (2026).

The activation energy (E_a) versus conversion degree (α) values for the dehydration and decomposition stages are shown in Figure 5.

Figure 5 - The calculated E_a/*kJ mol^{-1}* as a function of α to the dehydration stage and decomposition stage.



Source: Elaborated by the authors (2026).

For the dehydration stage, we can see that there are tendencies of the experimental fit to maintain the same features. So this indicates that kinetic dehydration occurs in the same way for every extension of conversion degree (α) of both mass samples. The relatively lower activation energies obtained might be attributed to the effect of weak bonds among the water and organic matter.

In the other side, the activation energy calculated to the decomposition stage of the aerobic sludge, shows variation on the conversion degree (α), but for both was not observed significant variation. For anaerobic sample, the kinetic behavior is higher that aerobic sample.

This difference between them can be ascribed to the characteristics of the samples during the first stage of the thermal decomposition, as observed in the DTG curves. In this curves it is possible to see for the anaerobic sample that this shift towards higher activation energy, was probably caused by the effect of the kinetics of the decomposition, which can be suggested as resulted of a delayed degradation.

4 CONCLUSIONS

In the present study, were evaluated two sludge samples and also their different contents of biodegradable matter. The results obtained with FTIR provide an important information concerning the organic matter types present in the sludge samples. Nevertheless, thermogravimetry (TG/DTG) curves provided previously unreported information concerning the thermal stability under carbonic gas atmosphere. The obtained results by TG/DTG about the pyrolysis can be considered as one of the most viable alternatives for the disposal of waste, but however a feasibility study is necessary, considering the cost-benefit of this exploration. Also, the considerations carried out by TG/DTG curves on the thermal behavior of organic matter are important because the thermal evaluation can determine it is quantity. The atomic absorption spectroscopy analyses revealed that the metal ion lead was detected in two samples, but are in agreement with the establish limits of environmental orientations by current legislation in Brazil. Furthermore, in this work was verified that there are different ions in these samples, and it application in the soil needs to be monitored to avoid the contamination by them or excessive availability in agriculture, which can be harmful to water sources and groundwater waters. Finally, in the present research, the kinetic parameters were calculated using the eqs. 3-6, from three TG/DTG curves obtained. Besides, the kinetic information is important for the study on large-scale in pyrolysis reactors, with which it is possible to predict the reactions. The values of activation energy for dehydration stage have the same feature, while the first thermal decomposition stage indicates different behaviors.

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