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Thermal behavior of residues (sludge) originated from Araraquara water and sewage treatment station

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Abstract The number of the cities with canalized water and sewage treatment stations has increased lately and consequently having in mind the great concern on environment preservation and the quality of the water used by society. However, these stations are nowadays causing another kind of problem: a huge quantity of sludge as residue. Due to the implication of the residue on the environment and, consequently, to human life quality, performing of an accurate investigation about the components of such sludge, as well as the thermal stability of this residue in the environment become necessary. This paper presents a study on sludge from water and sewage treatment station, as well as the thermal characterization of residue. Such study was performed through FTIR, atomic absorption, thermoanalytical (TG/DTG, DTA) techniques, that made it possible to observe that the main components of the sludge are clay, carbonates and organic substance, presenting a low rate of metals and a unique thermal behavior since the sludge from the treatment station has a higher thermal stability.

Keywords Residue · Sludge · Sewage · Thermal stability

Introduction

In the past century there was a low demand of water due the small population concentrations. Along with the disorganized population rise in the past decades, the consumption and the search for water have considerably increased. However, the pollution sources and difficulties in handling the residue of human activities have also increased. In 2000, in Brazil, around 10 billions of liters of domestic and industrial sewage was thrown straight to rivers without any sort of previous treatment, causing severe problems to health and environment [1, 2]. The necessity of residual water treatment is widely known, but due to the lack of resources, these actions are usually ignored.

The biggest urban centers created Sewage Treatment Stations (STS) in order to solve such problems. However, the treatment ends up causing another problem to society and the environment: the huge amount of sludge originated from the STS and the Water Treatment Stations (WTS).

A great quantity of sludge is daily produced in several cities [3–5] and normally this sort of residue is taken from it original place by trucks and thrown in controlled landfill or directly into the water (the WTS example). The STS sludge, when disposed in a controlled landfill, is usually covered with earth and urban garbage; however, the soil is not always water impervious or has a drainage system for the percolated liquids, which might cause infiltrations that will pollute subterraneous water [3]. This creates a hard problem once this residue might have simple oxides in its composition—as the sludge from the WTS—to potentially toxic elements as As, Cd, Pb, Cu and Mo, and pathogenic substances as protozoan, bacteria and virus if originated from STS.

Although these sludge disposal solutions may bring a momentarily tranquility feeling, they might cause afterwards severe environmental problems. The recycling [2, 4–6] is the best way from the economical and environmental view among the present solutions. As ways of reuse of the residue it is possible to highlight agricultural fertilizer (in its controlled form) [7], as a content in cement production [3]

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and general earthenware (bricks, tiles, pavement) and even its combustible conversion [4, 5, 8]. However, in order to give the right destination to the sludge it is first necessary to know its composition as well as its thermal stability. Therefore, it is crucial a detailed study on this sort of residue to know its components, its environment behavior and so evaluate the best alternatives for reuse and disposal.

Objectives

The purpose of this work is the study and the characterization of sludge from a water and sewage treatment station in the city of Araraquara, São Paulo State, Brazil.

Experimental

The sludge samples from the Water Treatment Station (WTS) and the Sludge Treatment Station (STS) were taken from Water and Sewer Department (DAAE), the organization that manages the sanitary measures in Araraquara. After this, the samples were homogenized and underwent a drying process during 4 days in an oven at 55 °C. The resulting solid was ground and sieved with a diameter of 250 μm called to work sample. For the atomic absorption spectrometry readings, the solid samples were digested using nitric acid and hydrogen peroxide; 2 g of the work 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, adding 5 mL of 30% H_2O_2 in every 30 min up to the opening of the sample. After cooling, the samples were filtrated and transferred to a 100 mL volumetric balloon and completed with water.

The other techniques used to research the sludge composition were: FTIR, atomic absorption spectroscopy (AAS) and simultaneous TG/DTG/DTA, in order to verify the thermal behavior of the residue.

Results

Infrared region absorption spectra, Figs. 1 and 2, allowed identifying possible compounds present in the sludge from STS and WTS. The results obtained are presented in Table 1.

The absorptions bands concerning the O–H stretchings might be given to the hydration water and N–H, C–H, the amine e-methyl present in the organic matter (cellulose, lignin and humic substances precursors). The possible oxides Si, Fe and Ca present are due to the fact that raw

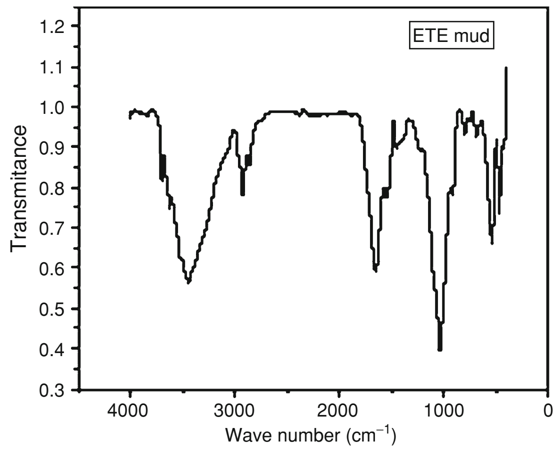

Fig. 1 Spectra absorption in the infra-red region of sludge STS

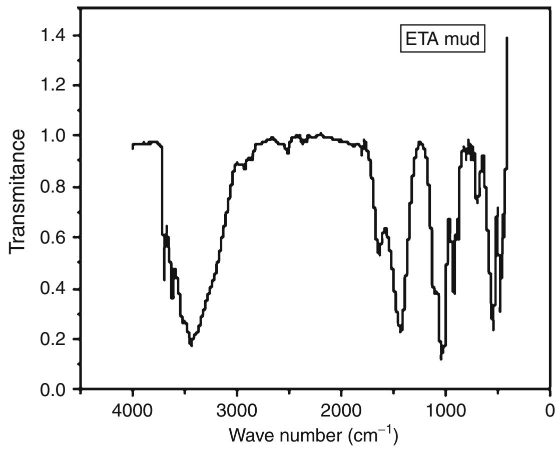

Fig. 2 Spectra absorption in the infra-red region of sludge WTS

Table 1 With the possible functions and substances present in the samples

ν/cm^{-1}	Vibration	Groups or functional components likely	References
3670–3080	O–H e N–H	Water and amine, bridges of hydrogen in phenols and acid or alcohol	[12–15]
2848, 1456 e 2900	C–H	Methylene aliphatic of humic acid or lignin	[12, 13]
1646	C=O	Amides and/or carboxilatos	[13]
1425[a]	C–O	Carbonates	[12, 13]
1228	Si–O	Sílica	[13]
875[a]	Fe–O	Iron oxide	[12]
707[a]	Ca–O	Calcium oxide	[12]

[a] Only for sludge WTS

Table 2 Concentration (mg/kg) of the metal samples of sludge STS and WTS

	Zn	Pb	Ni	Fe	Mn	Cu	Cr	Al
Sludge STS	9.9	nd	5.2	67.1	12.5	42.05	0.05	0.35
Sludge WTS	7,95	nd	4.9	54.6	5.08	23.35	0.45	0.2
CETESB earth and water	60	17	13	–	–	35	40	–
EMBRAPA Composto de lixo	1500	500	100	–	–	500	300	–

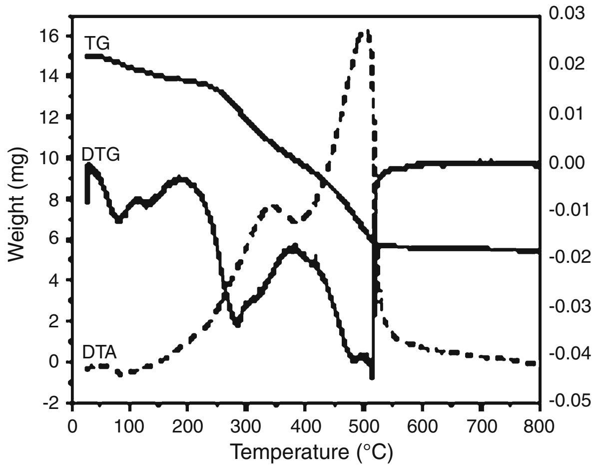

Fig. 3 Curves TG/DTG and DTA of sample sludge STS (air atmosphere, 20 °C/min)

water was collected straight from a pre-treated water, bringing along a large amount of suspension particles (sand and clay) and due to the reagents used in the process of flocculation ($FeCl_3$ and Ca).

Table 2 presents the metal concentrations (mg/kg) in the sludge samples from STS and WTS and also some values found in the literature [9, 10].

The obtained results for the metal concentration were similar to both samples, except for Cu, Mn and Cr concentrations. However, both samples showed a metal concentration inferior to Ambient Sanitation Technology Company—CETESB (water and soil) and Brazilian Company of Farming Research—EMBRAPA (garbage) orientations.

Figures 3 and 4 present the TG/DTG and DTA curve for the sludge samples for STS and WTS, obtained at 20 °C min^{-1} heating rate in synthetic air atmosphere. Through the comparison of the curves of the two samples, it was observed that the organic matter degradation happens at around 150 and 520 °C for both samples, although the sludge sample from the STS shows an organic matter level superior than the sludge from WTS; this fact is probably due to domestic effluents rich in organic matter. The WTS sludge presents in its composition inorganic substances as clay [11] and carbonates [11], which interferes directly in its thermal

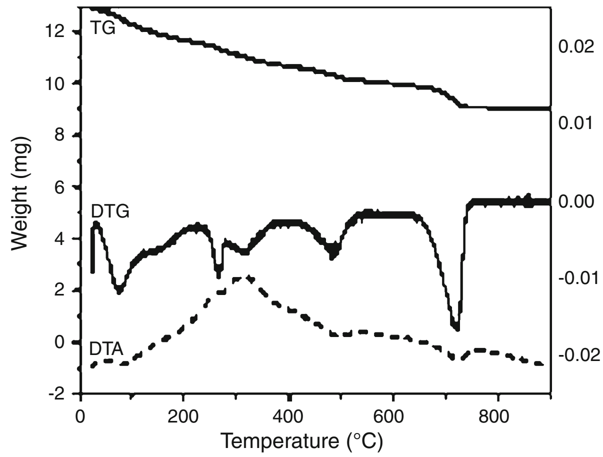

Fig. 4 Curves TG/DTG and DTA of sample sludge WTS (air atmosphere, 20 °C/min)

Table 3 Results of abtained through the curves TG/DTG and DTA for sludge STS

Temperature/°C	Δm/%	Event of decomposition	Peak DTA
180	7.5	Dehydration	Endo
180–520	54.5	Combustion of organic matter	Exo

Table 4 Results of abtained through the curves TG/DTG and DTA for sludge WTS

Temperature/°C	Δm/%	Event of decomposition	Peak DTA
130	6.3	Dehydration	Endo
130–530	15	Combustion of organic matter	Exo
240–280	–	Loss of water content of goetite (FeO (OH))	Endo
430–530	–	Loss of water content of caulinite ($Si_2Al_2O_5$ $(OH)_4$)	Endo
640–750	8.4	Decomposition of carbonates	Endo

stability, since the carbonate degradation only happens after 640 °C [11], as it can be seen in Fig. 4.

Combined with the TG curve with its derivative (DTG) and its respective DTA curve, it is possible to analyze each sample decomposition step, identifying what happens in each of them.

The results obtained through the analyses of the curves above are shown in Tables 3 and 4.

It is possible to observe that the STS sludge is made by a large amount of organic matter than the WTS sludge, which causes high energy liberation during the combustion process (DTA peak). The WTS sludge sample showed mass loss up to 750 °C, due to the presence of carbonates whose existence was proved through qualitative testing. The loss of water content of goethite (FeO(OH)) and caulinite ($Si_2Al_2O_5(OH)_4$) were attributed to the comparison with the work of OLIVEIRA [11], respectively Tables 3 and 4.

Conclusions

The results obtained through the FTIR analyses, along with the metal quantitative analysis by using atomic absorption technique and completed by TG/DTG and DTA curves provided important information concerning the STS and WTS sludge composition, as well as its thermal behavior.

The metal analyses showed that this type of residue presents different compositions; the STS sludge is rich in organic matter, resulting in a smaller thermal stability, whereas the WTS sludge has, besides organic matter (in lower rates), a significant amount of oxides and carbonates, causing the residue thermal instability to increase.

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