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Thermogravimetric Analysis Of Waste Sludge From Tannery

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ABSTRACT

Thermogravimetric analysis is an excellent tool in characterizing materials subjected to thermal treatment. Solid waste sludge generated in leather tanning industry is taken for thermal analysis in this study. After characterizing the sludge physically and chemically, thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTGA) were carried out in the temperature range of 50-1250°C. The TG and DTG profiles were interpreted and parameters like rate constant, pre exponential factor and activation energy were determined. Such an analysis will be useful in thermal treatment of sludges as in the raw form or mixed with a carrier like clay to form products like bricks.

KEYWORDS

Thermogravimetric analyzer;
Thermal analysis;
Environmental analysis;
Tannery sludge;
Waste management.

INTRODUCTION

The generation of solid wastes such as sludges from various industrial operations become one of the most serious environmental problems facing the entire world. Leather tanning is one of the notable emerging industrial sectors in the developing countries like India. The treatment of effluents from tannery involves the processes like coagulation, precipitation and subsequent biological treatment. As the amount of sludge produced by such waste water treatment plants increase, there is a need for safe reuse and effective disposal. The thermal treatment of either the sludge alone or along with clay mixture[1-3] to form useful products like fired bricks or tiles may be considered like an interesting route to deal with.

In environmental analysis, many thermal analytical techniques have been applied to characterize or to study thermal degradation of waste. Nevertheless, the lack of any standardization impedes the comparison of results from existing analytical techniques. Among them, thermogravimetric analysis (TGA) is based on the weight loss by a solid waste under programmed heating in a controlled atmosphere. The rate of weight loss that occurs in a sample is the basis for differential thermogravimetric analysis (DTGA). Solid waste materials can be subjected to thermogravimetric analysis for any one of the following reasons: To study the devolatilisation, pyrolysis profile[4-7], to check the thermal stability[8], and to check the possibility of utilization as fuel[9,10]. Studies were also reported in literature about the utilization of TGA data used in monitoring the stabilization process for waste activated sludge under aerobic[11] and anaerobic[12] conditions. TGA when coupled with X-Ray diffraction and NMR studies will provide sufficient information about the structural characteristics of the material[13-15]. Coupled with instruments like FTIR and mass spectrometry, TGA analysis will be a useful tool to predict the information about the evolution of the evolved substance[16-17].

In the present investigation, the sludge obtained from the waste water treatment of a tanning industry is considered for thermal analysis. The paper describes the thermal degradation of the sludge in a thermogravimetric analyzer. The technical information including the kinetic parameters obtained in this study will be highly useful when the sludge alone is subjected to thermal treatment in an incinerator or when it is mixed with carrier like clay material and subjected to thermal treatment in kiln to get products like bricks, tiles etc.

THEORETICAL

Origin of tannery sludge

Tanning process employs a series of chemical and mechanical operations to convert raw skin into leather. It also needs large quantities of water, sodium sulphide and other chemicals. Chrome tanning and vegetable tanning are the most common methods of leather processing in industrial practice. Among them chrome tanning which utilizes chromium salts for tanning of hides is more preferred because of the hides resulting with better mechanical strength and hydrothermal resistance. High rate of penetration of chromium salts in to the interfibrillar spaces of the skin also makes the chrome tanning superior to the other one. The poor efficiency of the operations, mishandling and organic matter from the skin contributes to the pollution load in the resulting waste water. The effluent from such tanneries consists of grease, chromium hydroxides; debris from hides is subjected to coagulation/precipitation and biological treatment. A schematic view of the various operations involved in tannery waste water treatment process where the sludge is originated is shown in figure 1.

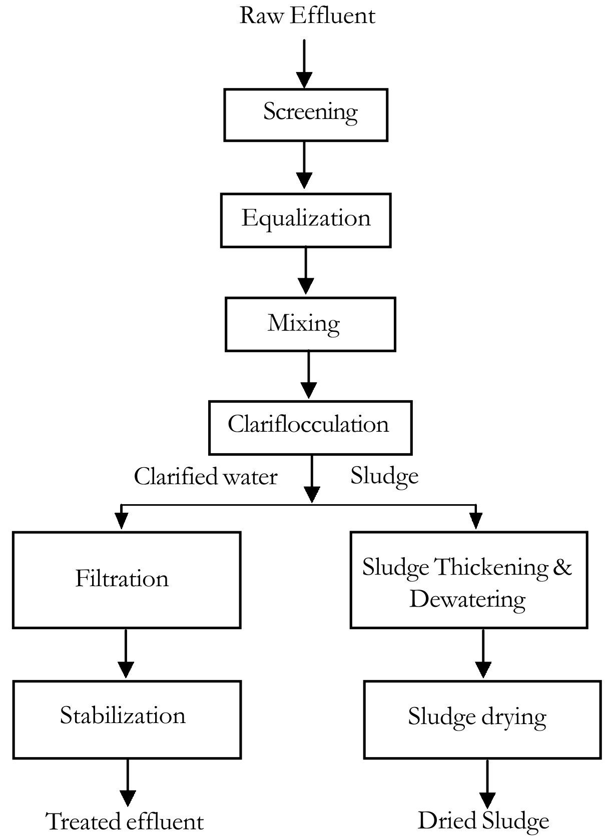

Figure1: Overview of the origin of sludge in tannery

Thermogravimetric analysis

Thermogravimetric analysis is a technique by which mass of a sample is measured as a function of temperature while the substance is subjected to a controlled temperature program. The mass variation with time (t) or temperature (T) is presented graphically as TG curve. Derivative or differential thermometry (DTG) is a technique that yields first derivative of the TG curve with respect to either time or temperature. The DTG curve is graphical representation of rate of mass depletion with time or temperature.

It is possible to calculate a theoretical TG curve if the kinetic mechanism and parameters are known, on the assumption that heat transfer is instantaneous and no temperature gradient exists within the sample. Thus the kinetics of most of the reactions under isothermal conditions is given by equation 1.

$$\frac{d\alpha}{d\alpha} = k\,f(\alpha) \tag{1}$$

Where α is the fraction reacted in time t and is equal to $(w_i - w_t)/(w_i - w_f)$. Here w_i is the initial weight of the sample, w_t is the weight at time t, and w_f is the final weight of the sample; k is the rate constant. The various forms adopted by the function (α) and its integrated forms $g(\alpha)$ have been discussed elsewhere. The temperature dependency of the rate constant follows the Arrhenius equation

$$k = A\,e^{-E/RT} \tag{2}$$

where T is the absolute temperature, A is the preexponential factor, E is the activation energy, and R is the gas constant. For linear heating rate,

$$T = T_0 + \beta t \tag{3}$$

From equations 1 to 3 we can establish

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} e^{-E/RT} dT \tag{4}$$

Equation 4 is the characteristic equation of the DTG curve, which when integrated yields equation of the TG curve. If the function $f(\alpha)$ is known, integration of the left-hand side of the equation is straight forward and gives the associated function $g(\alpha)$. The integration limits are between the initial and final temperature range over which the TG curve is observed, but they do not influence the shape of curve too greatly. The kinetic mechanism i.e., the function $f(\alpha)$ or $g(\alpha)$, however determines the shape of the curve.

EXPERIMENTAL

Sample preparation and characterization

The dewatered and open air dried sludge samples were obtained from the effluent treatment plant of tanning industry located in Tamilnadu state, India. The samples of the sludge were dried at a temperature of 105°C until the net weight was constant. The dried samples were ground in a ball mill for 30 minutes to reduce the size of large and uneven particles and directly used in the study. Homogenized sludge samples were used on dry basis for chemical analysis. Analytical reagent (AR) grade chemicals were used. The samples were analyzed in triplicate and the results were averaged. The pH was determined using a double distilled water suspension of each mixture in the ratio of 1:10 that had been agitated mechanically for 30 minutes and filtered through Whatman No.1 filter paper. The average particle size was determined by cumulative analysis using a sieve shaker with Taylor's standard screens (TSS). Heavy metal constituents were analyzed using Thermosolar 2ASS-spectra atomic absorption spectrometer (AAS).

Thermogravimetric analysis

The thermogravimetric analyzer (Perkin Elmer TGA7 analyzer) used for thermal analysis on tannery sludge is given in figure 2. The platinum crucible was used for efficient heat transfer between thermocouple and crucible and minimizes thermal loss. The specification of the equipment used is provided in TABLE 1. Dried sludge sample, 13 mg with an average particle size 0.2 mm is used, and the reproducibility of the runs is also tested. The assays were performed in a static atmosphere of air, using a heating rate of 50°C / min from the ambient atmosphere to 1235°C.

TABLE 1: Parameter range of thermogravimetric analyzer used

Parameter	Measurable range
TG measurement range	200 mg
TG sensitivity	0.2 mg
DTA measurement range	+/- 1000mV
DTA sensitivity	0.06 mV
Programmable rate	0.01-100ºC
Sample pan volume	45 ml
Atmosphere	Air, inert gas, Oxygen
Pure gas flow rate	0-1000 ml/min

Figure 2: Pictorial view of thermogravimetric analyzer

RESULTS AND DISCUSSIONS

The physical and chemical characteristics of the sludge are given in TABLE 2. The sludge appears to be grayish white in color and agglomerated fine solid in form. It pH varied from 8.5-9.2. The average particle size of the processed sludge sample is 0.2 mm which is based on cumulative distribution of particles represented in TABLE 3. The TGA and DTGA spectrums of the sludge are shown in figures 3 and 4. TGA curve (Figure 3) consists of three characteristic profiles: a) gradual weight loss up to 700°C corresponds to a weight loss of 29%, b) intensive 21%weight loss within a short temperature range of 700-815°C c) relatively stabilized profile beyond 850°C with negligible weight loss. The three regions of weight loss in TGA indicate the presence of different types of materials with varying molecular weights.

TABLE 2: Physio-chemical characterization of tannery sludge

Property	Value
pH	8.5-9.2
Color	Grayish white
Appearance	Agglomerated fine solids
Density	860-880 kg/m^3
Loss of Ignition	43-45%
Chemical constituents	Calcium salts, Ferrous salts, Aluminium salts and debris from hides

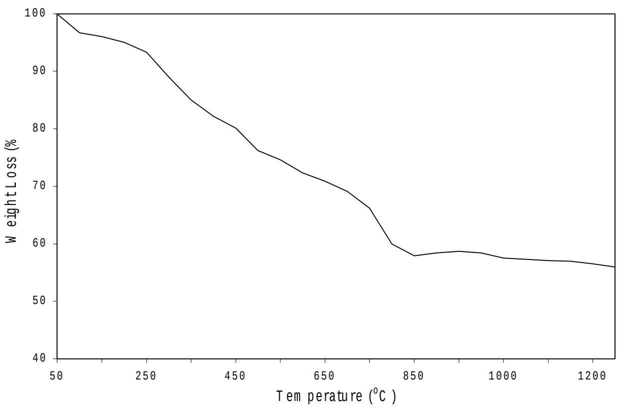

Figure 3: TGA Spectrum of tannery sludge

TABLE 3: Particle size distribution of tannery waste

Particle size (mm)	Cumulative mass Fraction
2.18	0.152
1.3	0.35
0.45	0.544
0.256	0.664
0.196	0.67
0.143	0.84
0.088	0.886
0.063	0.968
0.047	0.982
0.044	1

The DTGA profiles of sludge sample comprise a number of peaks and vary depending on the characteristics of the sludge. The DTG profile (Figure 4) starts with a peak before temperature reaches 125°C which may be due to the inherent moisture content of the sludge. In the temperature range 200-600°C, two different peaks are observed in the DTGA curve which characterizes the abundant release of volatile matter, which is similar to studies carried out with other sludges. The first peak centered at 300°C might be due to decomposition and devolatilisation of less complex organic structures which is a larger fraction. The second peak at 525°C was caused by decomposition of more complex organic structures corresponding to a smaller fraction.

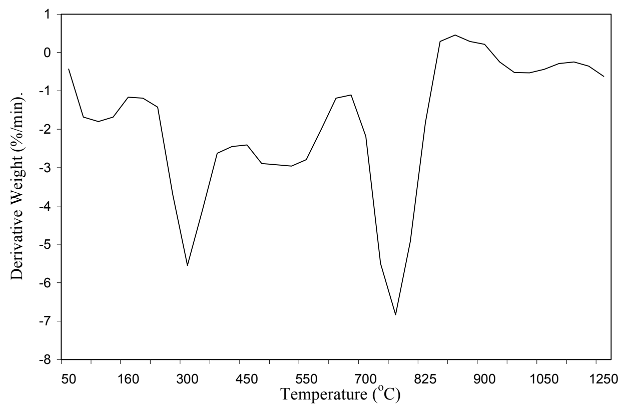

Figure 4: DTGA Spectrum of tannery sludge

This is reasonable because the tannery sludge happens to contain organic material including residues of hides and fleshes.

The most intensive peak of DTGA curve corresponds to temperature of 775ºC is possibly due to the decomposition of inorganic compounds such as calcium carbonate, ferrous sulphate, aluminum hydroxide etc. The rate of mass loss beyond a temperature of 850ºC is negligible (<3%). At the maximum thermal treatment temperature (1250ºC), the residue percentage is about 56%. The amount of residue depends on the presence of organic materials (corresponds to physical volatilation) in sludge as well as the amount of inorganic materials (corresponds to phase and structural change).

The weight loss or devolatilisation can be modeled as a first order process given by equation 5.

$$-\frac{dm}{dt} = k(m_i - m_{i\infty}) \qquad (5)$$

Where m_i and $m_{i\infty}$ are the mass of the unburnt mass of the 'i' fraction at each instant and the unburnt mass at the end of the peak respectively, k is a constant follows the Arrhenius equation(2). A reasonable fit to the devolatilisation data is obtained with the above equation and corresponding Arrhenius plot for the two high reactive zones (190-375ºC and 700-815ºC) are given in figure 5. Peak shifts in DTGA and kinetic parameters obtained from the Arrhenius plots are presented in TABLE 4.

TABLE 4: Interpretation of TG, DTG and arrhenius plots

Parameter	Value
Intial sample mass (gm)	13.27
Total residual mass	56
Temperatures of DTA M axima (ºC)	300, 775
For the first reactive temperature zone	
Activation Energy, E (J/Kgmol)	2583
Pre-exponetial factor, A (s^{-1})	0.01122
For the second reactive temperature zone	
Activation Energy, E (J/Kgmol)	3266.5
Pre-exponential factor, (s^{-1})	0.00083

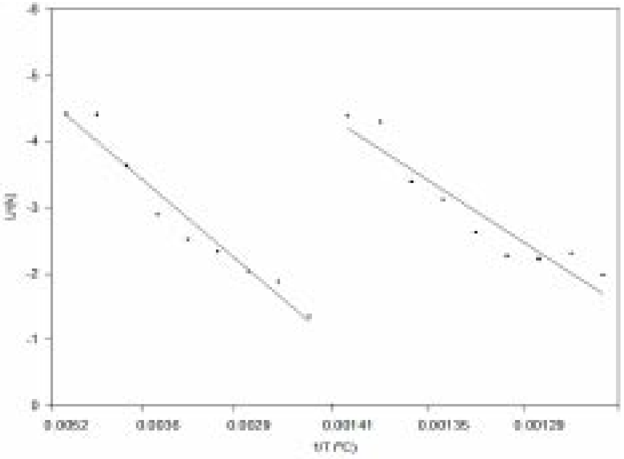

Figure 5: Arrhenius plot for the reactive temperature zones

CONCLUSION

The study deals with the thermogravimetric analysis of sludge from tannery industry at stipulated experimental conditions. The maximum weight loss (21 Wt. %) based reactivity occurs in the temperature region of 700-815ºC. Three regions of weight loss in TGA and corresponding characteristic peaks in DTGA indicate the presence and evolution of different types of materials and corresponding morphological changes in structure of the material. The interpretations obtained from the TG profiles and estimated kinetic parameters for the two high reaction temperature zones will be useful for strategic design of sludge management when thermal treatment is involved.

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