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Thermal analysis for the evaluation of the organic matter evolution during municipal solid waste aerobic composting process

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Abstract

A study aimed to monitor the composting process and to evaluate the effectiveness of indicators able to define the stability of a compost obtained by mixing municipal solid waste (MSW) and vegetal waste, was conducted. For this reason, composting process lasting 3 months, was monitored by chemical and thermal analysis. Total organic carbon (TOC), total extractable carbon (TEC) and humic and fulvic acid carbon (HA and FA, respectively) were determined after extraction, fractionation and analysis of organic matter from samples collected during the composting process. Differential scanning calorimetry (DSC), thermogravimetry (TG) and the first derivative of the TG (DTG) were simultaneously performed in oxidizing conditions on grounded compost samples and HA extracted. Thermoanalitical data resulted to be useful in integrating quantitative information coming from chemical analysis of humified fraction of compost organic matter. Particularly DSC curves allowed to distinguish between well and poor stabilized organic matter, and information deriving from weight losses, registered by the TG and DTG curves, enable to individuate the evolution state of the organic matter and therefore its stability.

Keywords: Compost stabilization; Humification parameters; Thermogravimetry; Differential scanning calorimetry

1. Introduction

The rapid spreading of the composting industries has caused an increasing necessity to follow the composting process with suitable parameters able to evaluate compost maturity and the quality of its organic components. Many parameters have been proposed for the evaluation of compost stability, with varying degrees of reliability and technical complication, including chemical tests, microbiological assays and the determination of the humified organic matter; but the analytical determination of all these parameters was often complicated [1–3]. Given the complexity of the biological events, the many interfering factors and the mixture heterogeneity in the compost, it is not surprising that the results are frequently contradictory. On these bases, it is difficult to build a general and complete theory for the organic matter evolution during composting and the need of gathering further scientific data arises [4,5]. Insofar it is important to evaluate the organic matter evolution during the composting process by simple, fast, relatively inexpensive yet reliable methods. Particularly thermal analysis, such as differential scanning calorimetry (DSC) and thermogravimetry (TG), seem to be useful for the characterization of the compost organic matter, because of their rapid determination and simplicity as well. They are based on a programmed heating of the samples in controlled atmosphere which finally provides qualitative and quantitative information regarding the compost humic matter content. These methods appear promising since they could be used to integrate the information obtained from the chemical parameters used to characterize organic matter of compost, peat, and soil [6–9]. However, most of the thermal studies related to the organic matter evolution during the composting process, compare thermal data from different compost [10], or characterize the thermal evolution of the humic acid extracted from the composting materials [1]. Insofar could be interesting to follow and analyze at the same time the organic matter and the humic acid thermal evolutions during the composting process.

Then the aim of this work was to give a contribution to a deeper knowledge of the composting process and to ascertain if the thermal indicators are able to describe the degree of

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the process development and if it is possible to compare and integrate them with chemical data currently used to define compost quality and stability.

2. Materials and methods

2.1. Composting of municipal solid waste

The organic fraction of selectively collected municipal solid waste (MSW) and vegetal waste (containing leaves, grass clippings, and shredded bark 1:1:1, v/v) at a ratio 1:1 (v/v), were composted in the city refuse treatment plant of Carpi (Modena, Italy). The trial was followed for 100 days and the process typology was a dynamic and aired type 30 days long followed by a static and not-aired one 70 days long. The process development was monitored checking the temperature during composting. Readings were taken daily at three depths in the piles (20–50–80 cm) during the first month and weekly during the not-aired phase. The composting process proceeded with an initial increase in temperature up to 60 °C during the first month that represented the “active phase” of the process. After about a month the temperature began to fall due to slowing down of the oxidizing process carried out by the microflora present in the organic matter. This second phase represented the “curing phase” of the process. Homogeneous replicated samples of approximately 3 kg in different stages of evolution were randomly collected from different points: every week during the “active phase”, and every 2 weeks for the rest of the composting process “curing phase”. Moisture content of compost samples was measured every week and kept at a level of 40–50%. Smaller subsamples coming from 3 kg samples were dried at 65 °C then ground and sieved. Particles smaller than 2 mm in diameter were used for chemical and thermal analyses.

2.2. Extraction and fractionation of the organic carbon

For the analysis of the total extractable carbon (TEC (%) d.m.) 2 g of the sample were treated with 100 ml of a 0.1N $NaOH/Na_4P_2O_7$ solution under N_2 for 48 h at 65 °C in a thermostatic bath and at 80 oscillations/min. After centrifugation the supernatant solution was filtered through a 0.45 μm Millipore filter and then stored under N_2 at 4 °C [11]. The humic and fulvic acid carbon (HA (%) d.m. and FA (%) d.m., respectively) were fractionated by acidification of 25 ml of the extract with 50% H_2SO_4 ($pH < 2$), separating the HA (precipitated) from the FA (in solution); the FAs were purified on a polyvinylpyrrolidone (PVP) column, and resolubilized with 0.1N NaOH [11]. The HA and FA fractions were then stored under N_2 at 4 °C until analysis.

2.3. Chemical determinations

Total organic carbon (TOC (%) d.m.) was determined by oxidation with potassium dichromate [11]. The determination of TEC (%) d.m. was carried out by mineralization of 10 ml of the extracts with 5 ml of 2N $K_2Cr_2O_7$ and 20 ml of 96% H_2SO_4 for 10 min at 160 °C. The concentrations of HA (%) d.m. and FA (%) d.m. were obtained by mineralization as described above on 10 ml of the humic extracts.

2.4. Thermal analysis

Compost samples dried at 65 °C for 24 h manually ground in agate mortar and sieved to 0.2 mm, and HAs lyophilized and freeze–dried, were analyzed for thermal analysis. All the analyses were performed on compost samples and HA collected and extracted at different times of the composting process:

- at the beginning of the composting process: time 0;
- after 28 days: end of the “active phase”;
- after 100 days: end of the composting process.

TG and DTG were carried out with a Mettler TG20 Termobalance, TA 3000 system. A calibration with trafoperm, nickel and isotherm contemporarily, followed by a check with nickel, was performed before the analysis. The following conditions were adopted for all TG and DTG analyses: heating rate of 10 °C/min from 25 to 800 °C, oxidizing atmosphere for static air, and samples weights of about 50 mg. DSC was carried out with a Mettler TA-STAR 821. A total calibration with indium/zinc, followed by a check DSC exo-indium, was performed before the analysis. The following conditions were adopted for DSC analyses: heating rate of 5 °C/min from 45 to 550 °C, oxidizing atmosphere for static air, and samples weights of about 10 mg. Measurements were repeated at least three times.

2.5. Statistical analysis

All the reported results are expressed as mean of three replicates. One-way analysis of variance (ANOVA) was carried out to compare the means of different treatments; where significant *F*-values were obtained, differences between individual means were tested using the least significance difference test.

3. Results

3.1. Humification parameters

The TOC concentration (% d.m.) clearly decreased during the first month of the composting process: during this phase, called “active phase”, thermophilic bacteria decomposed the easily degradable organic matter with production of CO_2, H_2O, and heat. Subsequently, following the decreasing rate of the organic molecules degradation, the organic matter maturation and stabilization began. This second period is called “curing phase”. Particularly during this phase (from 42nd to the 100th day) the TOC values found were not

Table 1
Changes in TOC, TEC, HA and FA (in %) referred to d.m. at 105 °C during the composting process

Number of days	TOC (% d.m.)	TEC (% d.m.)	HA (% d.m.)	FA (% d.m.)
0	40.88 a	8.76 a	5.02 a	1.13 a
7	33.33 b	8.89 a	5.09 a	1.18 a
14	26.41 c	9.09 a	5.16 a	1.30 a
21	23.54 cd	8.85 a	5.23 a	1.36 ab
28	21.51 de	8.50 a	5.36 a	1.51 bc
42	19.87 ef	8.47 a	5.95 b	1.51 bc
56	19.08 ef	8.51 a	6.04 b	1.63 cd
70	18.62 ef	8.63 a	6.03 b	1.70 d
84	17.75 f	8.65 a	6.25 b	1.65 cd
100	17.38 f	8.81 a	6.22 b	1.67 d

Data with the same letter within the same column do not differ significantly at the 5% level according to least significant difference test.

statistically different (Table 1). The TEC concentration (% d.m.) has been constant during all the process (Table 1). The HA concentration (% d.m.) to the contrary increased during the process, particularly at the beginning of the "curing phase" (Table 1); however, this increase represented a least percentage in comparison to the pre-existing humified fraction. The FA concentration (% d.m.), that is a small fraction of the humified substances, increased during the process, and reached constant values after the 56th day (Table 1).

3.2. Thermal analysis

TG and DTG compost thermograms showed in the 50–150 °C range a weight loss representative of the dehydration reactions (Figs. 1 and 2) [12]. Between 200 and 760 °C, the decomposition process occurred mainly in two steps. The 210–320 °C range, attributed to the combustion of the carbohydrates [13], the initial sample (time 0) showed a weight loss of 37.9% d.m., that decreased in the final sample (100 days) to 20.8% d.m. (Table 2). In the second step, 400–520 °C, the thermal degradation of the aromatic structures occurred [14,15] (Figs. 1 and 2). Finally, the thermograms were characterized by a modest weight loss in the 695–750 °C range, attributed to the carbonate thermal degradation [16]. During the composting process, the carbonates weight loss increased because of their concentration (Figs. 1 and 2). The weight losses recorded in the 200–695 °C range were of 69% d.m. (time 0), of 61% d.m. (28 days), and of 43% d.m. in the final sample (100 days) (Table 2). In particular, the progressive reduction of the carbohydrates was evident. In fact immature compost was characterized by a high carbohydrates component which tend to disappear in the stabilized compost; to the contrary, the aromatic components, which are typical compost constituents, did not vary in a signifying manner (Fig. 2).

Table 2
Weight losses (percentage of total sample weight) corresponding to the main peaks shown in the thermograms (Fig. 2) and the temperature ranges (°C) in which they occur

Number of days	200–695 °C	210–320 °C	400–520 °C	695–750 °C
0	69.119	37.892	30.462	3.385
28	61.350	31.651	29.369	6.439
100	43.000	20.848	21.593	7.173

The TG and DTG thermograms of the extracted HA, showed a weight loss between 60 and 105 °C, generally representative of dehydration reactions (Figs. 3 and 4). In the 230–385 °C range, corresponding to the thermal degradation of carbohydrates and other different substances, the weight loss rate $\Delta M/\Delta T$ progressively decreased as the composting process proceeded (Fig. 4). At the same time, the weight loss recorded between 520 and 650 °C, due to the dissociation and decomposition of aromatic structures and polynuclear systems of higher molecular weight [17], increased with the composting time (Table 3). This trend, according to other

Table 3
Weight losses (percentage of total sample weight) of the HA corresponding to the main peaks shown in the thermograms (Fig. 4) and the temperature ranges (°C) in which they occur

Number of days	200–695 °C	230–385 °C	520–650 °C
0	57.758	20.612	19.408
28	51.770	17.136	22.793
100	50.057	15.988	27.718

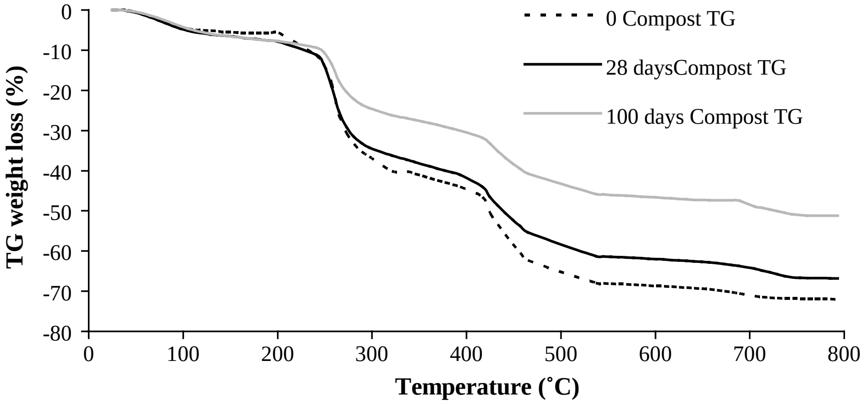

Fig. 1. TG curves of the samples collected at different times of the composting process.

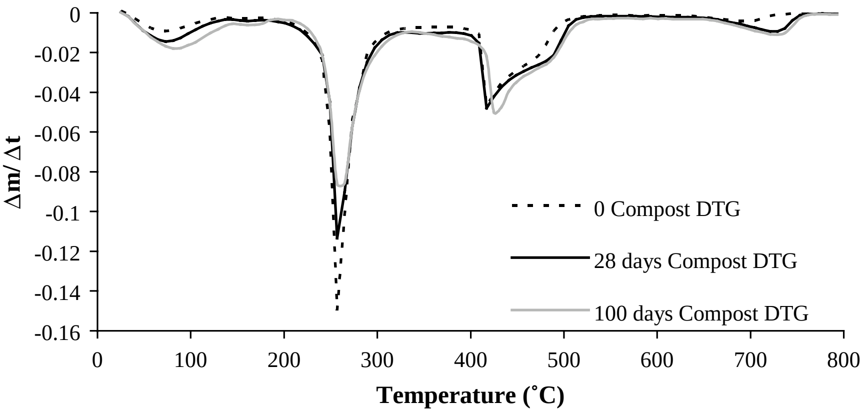

Fig. 2. DTG curves of the samples collected at different times of the composting process.

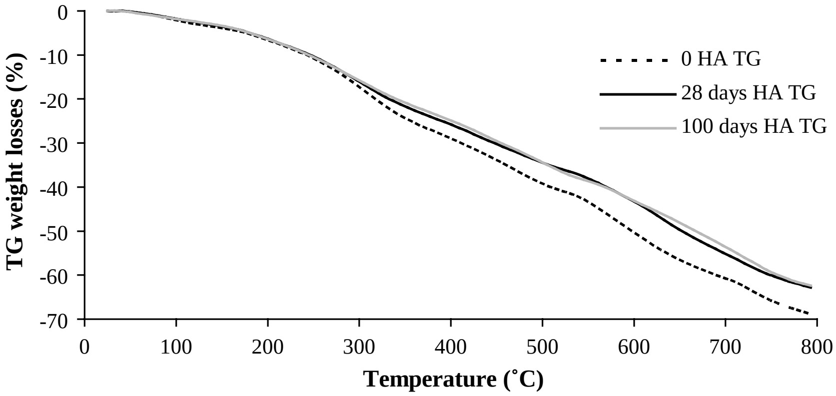

Fig. 3. TG curves of the HA extracted from the compost samples at different times of the humification process.

authors [18,19], suggest a progressive transformation of the biomass in the polyelectrolyte macromolecules referred to as humified matter. The observed differences in the HA thermal decomposition thermograms, as well as those present in the compost samples thermograms, underlined the different humification degrees, pointed out also by the TOC and HA evolution during the composting process.

The compost DSC curves were characterized by an endothermic peak near 97 °C, generally representative of dehydration reactions, and two distinct exothermic peaks (250–350 and 440–540 °C) which, in the kinetics of thermal decomposition and oxidation, indicated the thermal reactions of organic components characterized by different thermal stability (Fig. 5). As the composting process advanced, the intensity of the second exothermic peak increased, while the first one slightly decreased (Fig. 5). These exothermic reactions were associated with two distinct weight losses on the TG and DTG curves (Figs. 1 and 2). The presence, in the final compost sample (100 days) of a more intense peak in the 440–540 °C range could be a distinctive character of

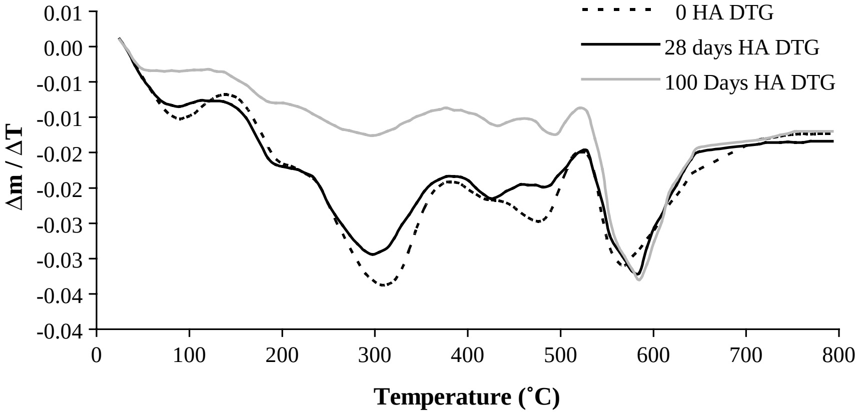

Fig. 4. DTG curves of the HA extracted from the compost samples at different times of the humification process.

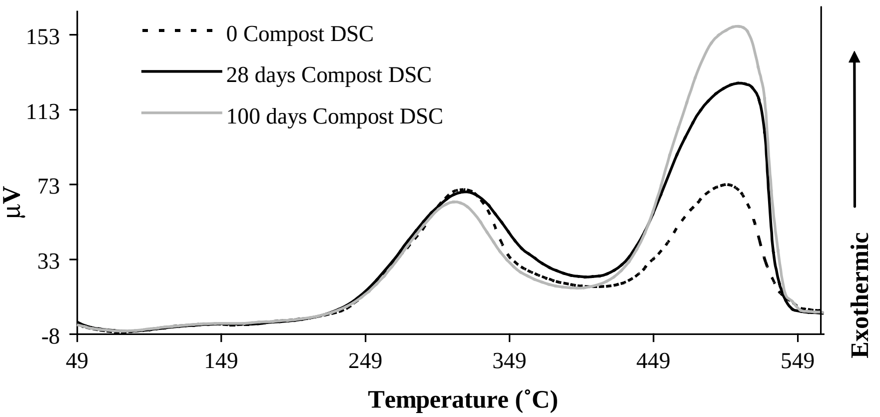

Fig. 5. DSC curves of the samples collected at different times of the composting process.

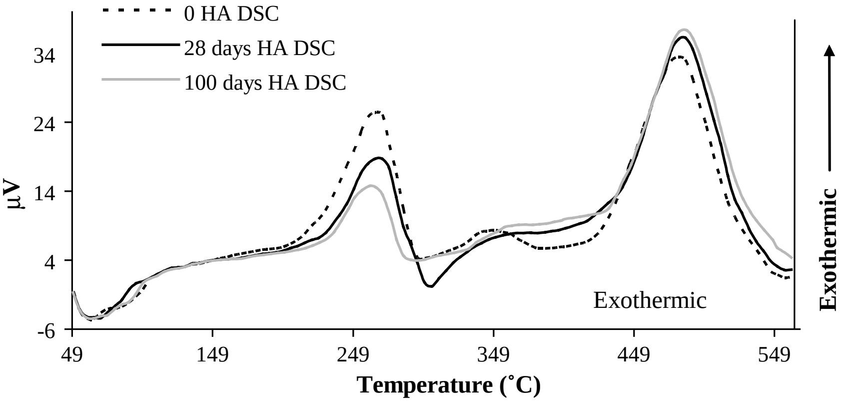

Fig. 6. DSC curves of the HA extracted from the compost samples at different times of the humification process.

humified organic matter. This trend could be related to an increase of molecular weight, stability, and aromatization degree during the composting process. Therefore the DSC curves analysis, according to other authors [1,10,13,20], could be used to evaluate the stability of the processing materials (Fig. 5). The DSC thermograms of the HA extracted showed the same trend: they were characterized by an endothermic peak at low temperature (55–81 °C), and two main exothermic peaks within 215–300 and 440–540 °C ranges (Fig. 6). The first exothermic peak, corresponding to thermal degradation of the carbohydrates, dehydration of aliphatic structures and decarboxylation of carboxylic groups, decreased during the composting process. The second one, representing the oxidation of the aromatic structures, the organic components with great thermal stability, slightly increased during the process (Fig. 6). Consequently, we refer an increasing thermal stability in the HA extracted with increasing of composting time.

4. Conclusions

Thermoanalytical data could be useful in integrating quantitative information coming from organic matter chemical analyses during composting process, giving an indication of the humification degree. In fact, in analogy with the chemical results (particularly TOC and HA evolution during the composting process) the thermal parameters based on compost and HA DTG thermograms, and compost DSC curves, were indicators of organic matter evolution during composting process. In fact the parameters based on compost TG and DTG thermograms showed a progressive thermal stabilization of the organic matter. Also, the thermal stability of the HA, noticed by the TG and DTG curves, increased with the progress of the composting. In particular, evaluation of DSC curves allowed to distinguish well and poorly stabilized compost. Well stabilized organic matter showed thermal oxidation kinetics characterized by a strong intensity of the second exothermic reaction, due to organic matter fractions having high thermal stability; while in poorly stabilized organic matter the second exothermic reaction showed a small intensity. Instead, for HA DSC curves intensity differences were smaller.

Therefore, we show that thermal analysis and thermogravimetry can be used as reliable and suitable techniques for the assessment of the evolution of the compost organic matter. Besides thermal analysis proves to be a very simple and reproducible technique, which could be applied to the whole sample, without pre-treatment.

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