



Spectroscopic, thermogravimetric and structural characterization analyses for comparing Municipal Solid Waste composts and vermicomposts stability and maturity



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HIGHLIGHTS

- Extensive comparison of maturity indexes among compost and vermicompost is assessed.
- Difference in intensity of peaks by FT-IR spectra between compost and vermicompost.
- Vermicompost TG curve had lower mass loss than compost, indicating higher stability.
- Low-temperature peak in vermicompost DSC curve proved greater maturity than control.
- SEM micrographs of vermicompost showed strong disaggregation compared to compost.

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ABSTRACT

This is the first-ever study of its kind for an extensive assessment and comparison of maturity indexes between compost and vermicompost that have been derived from Municipal Solid Waste (MSW). The spectroscopic (Fourier transform infrared spectroscopy: FT-IR), thermogravimetric analysis (TG), differential scanning calorimetry (DSC) and structural characterization (scanning electron microscope: SEM) were recorded. FT-IR spectra showed an increase in conversion of polysaccharides species and aliphatic methylene groups in vermicompost compared to compost as depicted from the variation of the intensity of the peaks. TG curves of final vermicompost showed a much lower mass loss when compared to compost, indicating higher stability in feedstock. SEM micrographs of the vermicompost reflected strong fragmentation of material than composts which revealed the extent of intra-structural degradation of MSW. These findings elucidate on a clear comparison between composts and vermicomposts in terms of maturity indexes for soil enhancement and in agriculture as organic fertilizer.

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1. Introduction

With the rapid expansion in urbanization, modern life style, consumption pattern and the imposition of stricter environmental laws, the production of Municipal Solid Waste (MSW) has been increasing dramatically in yesteryears. Due to the putrescible characteristics in posing serious threat to ecosystem functioning and continuous increase in MSW generation, solid waste management (SWM) has become an issue of growing global environmental con-

cern. In the reckoning of a few authors and in most cases, the common SWM practice which is adopted for MSW by several countries around the world is sanitary land filling (Norbu et al., 2005) and open dumping. From an ecological point of view, these waste disposal methods are unsustainable owing to the production of certain toxic substances and gases from MSW which may have potential adverse effects on the environment, health and biodiversity. Also, it was found that the total contribution of methane emission worldwide from landfills is about 3–19% (Gupta and Garg, 2009). In this context, the need for sustainable and cost-effective methods with promises of reducing the organic load on landfills and environmental impacts of improper SWM is greatly urged.

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Over the last two decades, composting emerges as an appropriate technology to alleviate SWM and it has been brought up to date to handle organic waste of different origins, including MSW (Castaldi et al., 2005; Petric et al., 2012; Gutierrez et al., 2015). Composting is an extensively recognized technology which involves the recycling of nutrients for plant growth and their re-use as an organic amendment for the enhancement of soil physical properties (Huang et al., 2005) owing to moisture reduction, pathogen inactivation and low processing cost (Aggelides and Londra, 2000). Recently, Soobhany et al. (2015a) found that vermicomposting considerably improved the decomposition and stabilization of organic fraction of MSW into an organic fertilizer. In contrast to normal composting, vermiculture involves microorganisms which are in charge for the biochemical break down of organic substances and earthworms for promoting aeration states, organic matter mineralization rate (Hanc and Vasak, 2015). In addition, the vermicompost is much richer in plant-friendly minerals, hormones/enzymes and biochemically enhanced over conventional compost owing to greater humification rate during vermistabilization (Hussain et al., 2016). It is known from previous research that vermicomposts derived from organic waste usually contain higher bioavailability of nutrients content (Soobhany et al., 2015b) with an increased level in humic acid as compared to their parent materials (Edwards et al., 2011). Additionally, sanitization of organic solid waste (Ndegwa and Thompson, 2001) and elimination of toxic heavy metals are enabled by an integrated composting-vermicomposting system (Soobhany et al., 2015a; He et al., 2016). But no past attempt concerning a broad assessment and comparison of stability and maturity indexes between MSW compost and vermicompost has been researched. Moreover, the physicochemical properties such as temperature, particle size, pH, electrical conductivity, bulk density, volatile solids, nutrient contents and organic carbon in composting employed to treat organic waste have been broadly researched (Nolan et al., 2011; Petric et al., 2012).

Besides these parameters, compost and vermicompost maturity can be evaluated by employing spectroscopic characteristics (Fourier transform infrared spectroscopy: FT-IR) (Ouatmane et al., 2000), thermogravimetric analysis (TG) (Smidt and Lechner, 2005; Zbytniewski and Buszewski, 2005), differential scanning calorimetry analysis (DSC) and structural characterization (scanning electron microscope: SEM) (Hussain et al., 2016). Thus, these spectroscopic, thermal and structural analyses could be used effectively to obtain comparative, complementary information and description on MSW composts and vermicomposts maturity. FT-IR analysis is a crucial qualitative technique for distinguishing the functional groups of organic substances and is usually utilized in the examination of soil organic matter, organic wastes and their compost (Amir et al., 2010). Thermal analysis (TG and DSC) are effective tools for exemplifying the end product in providing chemical characteristics of samples since they are straightforward, fairly cheap and steadfast methods (Zbytniewski and Buszewski, 2005; Wu et al., 2011). SEM analysis serves as a microscopic tool on various organic waste and composts where the surface morphology is clearly elucidated (Wan Razali et al., 2012). Generally, the application of these various maturity analyses will further give a comprehensive depiction and nature of the vermicompost as compared to compost (control) derived from MSW, in which case there is a lack of information regarding compost against vermicompost characterization using high-end equipments. Still, regardless of numerous studies on composting, no information has hitherto been found on these analyses for an extensive assessment and comparison of stability and maturity indexes between vermicompost and compost. The few studies that are available on vermicomposting maturity entailed spectroscopic analysis of vermicompost com-

pared to initial wastes. The search for an effective use of MSW vermicomposts as compared to composts in terms of best compost stability and maturity criteria is still under way. It should however be noted that this study was confined to the characteristics of the final composting and vermicomposting products. Therefore, in line with the actual situation and to enhance a reliable and easily manageable method for the determination of compost stability and maturity, the present study reports extensive investigations supported by FT-IR, TG, DSC and SEM analyses to identify the difference in MSW vermicomposts compared to its respective composts (control).

2. Materials and methods

2.1. Feedstock materials collection

The detailed method to generate the best compost and vermicompost from organic MSW was described by Soobhany et al. (2015a). In regards to appropriateness for vermicomposting, the organic waste from the Municipal Solid Waste (MSW) that were chosen were food waste, grass clippings, dry leaves and small branches, market waste, office shredded paper and newspaper, and cow dung. The organic waste was collected from the waste collecting trucks which consisted of mixed MSW such as kitchen waste, yard waste, paper waste, plastics, textiles, metal cans, glasses and others. To obtain the organic fraction of waste materials, the mixed MSW wastes were sorted manually. The finished compost which was employed for the research was compost from MSW which comprised of kitchen and yard wastes. The cow dung was provided by the agricultural farm of the University of Mauritius in Réduit. Cow dung was not the MSW fraction and it was added to the scenarios to balance the C/N ratio. Moreover, another purpose was that cow dung could aid as a bedding material for the earthworms. Three different compositions with dissimilar components of the organic fraction of MSW were opted and computed with the purpose of achieving a C to N ratio of 30 and moisture content of 55–60%.

2.2. Collection and culturing of earthworm biomass

Stock earthworms *Eudrilus eugeniae* (African Nightcrawlers) which were of different age groups were acquired from a vermicomposting building block of a local cowshed by disinterring into the composted cow dung. These earthworms were nurtured on partially decomposed cow dung mixed with leaf litter of *Litchi chinensis* in the laboratory which has a controlled temperature facility system. Perspex bin of sizes 450 × 300 × 450 mm were constructed for growing the cultures. Hatchlings were obtained from the incubation of fresh cocoons of stock earthworms *Eudrilus eugeniae* at 25 °C in laboratory. For the purpose of avoiding any contamination, the second generation of earthworms was utilized for the vermicomposting experiments. For the aim of this study, acclimatized juvenile and adult earthworms were unsystematically picked from the separately conserved cultures and used for the vermicomposting scenarios.

2.3. Experimental design

2.3.1. Mix calculation and preparation

The mix calculation and preparation of the mixtures was followed as per the procedure explained in Soobhany et al. (2015a). A total of six scenarios were set up wherein three experiments were for composting symbolized as S1 for food waste mix (ratio of 5:0.5:1 of food waste, dry leaves and paper), S2 for paper waste mix (ratio of 4:5:1 of market waste, cow dung and paper)

and S3 for yard waste mix (ratio of 2:2:1 of grass, cow dung and dry leaves) and the corresponding replicates for vermicomposting processes were S4, S5 and S6 for food, paper and yard waste respectively. Scenarios 1, 2, 3 were regarded as controls (mixture without the earthworms) and for comparison with the vermicomposting scenarios.

2.3.2. Composting and vermicomposting experiments

Composting experiments were conducted in 244 L (effective size of $0.65 \times 0.60 \times 0.90$ m of L \times W \times H) wooden in-vessel composters for Scenarios 1, 2, 3 and vermicomposting experiments (pre-composting followed by vermicomposting technologies) in 244 L wooden vermibins for Scenarios 4, 5, 6 in a manner detailed earlier (Soobhany et al., 2015a). Turning of the composting piles was done once in every 15 days till the end of the composting process. Vermicomposting experiments were conducted in wooden vermibins measuring $0.65 \times 0.60 \times 0.25$ m³ (Length \times Width \times Depth) and this gave an exposed top surface area of 0.39 m². For the period of vermicomposting, the depth of the pre-composted substrates in the vermibins decreased to 0.25 m. A most favorable worm stocking density of 1.60 kg worms/m² was employed in the setups for this experiment in order to attain the utmost bioconversion of the feed materials into earthworm biomass as earlier researched by Ndegwa et al. (2000). After 2 weeks of pre-composting, the composted materials were turned over to augment the aeration and disperse the heat that was generated during the thermophilic phase. In the 3rd week, 225 acclimated *Eudrilus eugeniae* (live-biomass loading of 0.624 kg) were inoculated into each of the particular vermibins (Scenarios 4, 5, and 6) which contained the pre-composted materials when the temperature steadily reached 30 °C i.e. after finishing the thermophilic phase. During the vermicomposting process, the moisture content of feedstock was retained at $80 \pm 5\%$ by periodic sprinkling of adequate quantity of tap water together with manual turning on a weekly basis so as to offer proper aeration to the earthworms. The total duration for the pre-composting and vermicomposting processes was 10 weeks. At the end of the vermicomposting experiments, the vermicast which was harvested as an apparent and particularly quantifiable product from the vermibins was termed vermicompost. The quantities of the composts and vermicomposts were recorded on a dry weight basis obtained by drying the samples to constant weight in an oven at 105 °C. The three types of composts generated from composting (controls) denoted as CS1 for food waste compost, CS2 for paper waste compost and CS3 for yard waste compost and the three types of vermicompost produced from the equivalent vermicomposting processes were VS4 for food waste vermicompost, VS5 for paper waste vermicompost and VS6 for yard waste vermicompost.

2.4. Experimental analysis

2.4.1. C/N ratio

The C/N ratio for the initial mix and final end products was computed by finding the percentage of total C and N which were analyzed using a EURO EA Elemental Analyzer on a dry basis. The dried samples were finely ground in a kitchen grinder (Philips Mixer Grinder HL7810/00750W) and 0.5–1.0 mg were weighed and used for the determination of total C and N.

2.4.2. Spectroscopic analysis: Fourier transform infrared spectroscopy (FT-IR)

The samples of MSW composts and vermicomposts were oven dried, finely crushed in a kitchen blender (Moulinex), and homogenized in an agate mortar. The functional groups in the composted products were examined by an FT-IR spectrometer (Bruker Alpha Platinum-ATR) in the spectral range of 4000–400 cm⁻¹ wavenum-

bers. FT-IR spectra of compost and vermicompost samples were recorded in the mid infrared area. In agreement of presentation and analysis, all the spectra were baseline corrected.

2.4.3. Thermogravimetric (TG) analysis

Thermogravimetric analysis (TG) was carried out using a TA Instrument (model TGA Q500 V6.7Build 203) after the samples were ground (10–20 mg) manually in agate mortar and sieved to 0.2 mm pore size. The analyses were performed on a dry basis using aluminum crucibles (60 μ L) in an inert nitrogen atmosphere (balance gas: Nitrogen 40 mL/min and sample gas: Nitrogen 60 mL/min). TG was done in a temperature range of 20–600 °C at a heating rate of 10 °C/min and the manometric pressure was kept at 101 kPa.

2.4.4. Differential scanning calorimetry (DSC) analysis

Differential scanning calorimetry (DSC) was performed on a DSC apparatus (DSC 200 F3 Maia). The finely ground samples (7–8 mg) were weighed in covered aluminum crucibles and thermoanalytical analysis was done under a reduced nitrogen atmosphere with temperature ranging from 0 to 300 °C at a rate of 10 °C/min.

2.4.5. Structural characterization: scanning electron microscopy (SEM)

For scanning electron microscopy (SEM) analysis, the samples were dried and finely crushed in agate mortar. 0.5 g of the ground samples were placed on aluminum discs of 12 mm in diameter and then left in an ion coating instrument. The compost and vermicompost samples were coated with gold ions for about 20 min. The coated stumps were positioned in SEM module (FEI Nova NanoSEM 230 with a field emission gun) which recorded their morphological structure at $\times 500$ magnifications.

3. Results and discussion

3.1. C/N ratio-index of compost and vermicompost maturity

A decrease in C/N ratio with time is an essential maturity index broadly applied for the maturity evaluation of compost and vermicompost. The C/N ratio of the initial mixing process and final compost and vermicompost for the six scenarios is shown in Fig. 1. In the present study and as evident from Fig. 1, the final C/N ratios of the MSW composts were in the range of 18.0–22.1 in all the in-vessels, depicting the overall decrease of 39.2% for CS1, 25.5% for CS2 and 24.1% for CS3 from the initial values. This decrease indicated a high level of stabilization in all the feed substrates. The cause of this fall in C/N ratio during composting processes could be regarded as being caused by microbial respiration due to which carbon is lost as CO₂ leading concomitantly to an increase in the proportion of total nitrogen of the medium. The final C/N ratios of the MSW vermicomposts were in the range of 15.0–16.2 in all the worm-worked vermibins (Fig. 1), depicting the overall decrease of 48.5% for VS4, 41.5% for VS5 and 45.1% for VS6 from the initial values. A diminution in C/N ratio of 37.13% in the vermicomposting of MSW with *Perionyx ceylanensis* Mich. was noted by Paul et al. (2011) which barely reflected the values obtained from this study. The extent of reduction in C/N ratio attained during composting and vermicomposting of MSW reveals its conversion into nitrogen-rich manure. The decrease in C/N ratio during vermicomposting agreed with previous report (Kaushik and Garg, 2003) thereby depicting advanced extent of organic matter stabilization (Gupta and Garg, 2009). Comparing the C/N of composts to that of the vermicomposts generated from MSW, it could be observed that a much higher decrease in this ratio was obtained in the vermicomposts which might be due to the addition of nitrogen con-

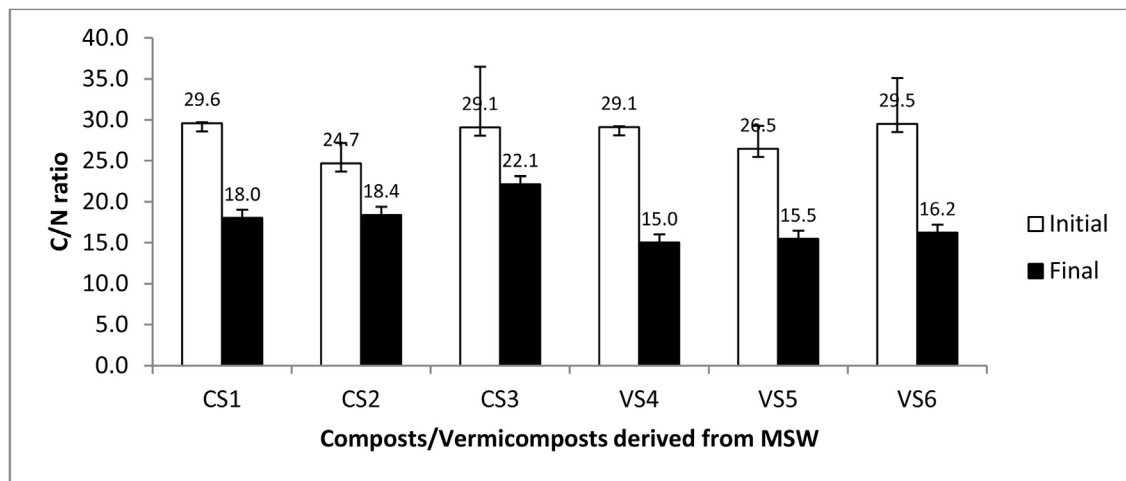


Fig. 1. C/N ratio of initial composting/vermicomposting mix and final compost/vermicompost.

tent by the action of earthworms as similarly reported by Suthar (2010). Also, Domínguez and Edwards (2004) reported that earthworms might mineralize organic nitrogen in the form of mucus, excreta, enzymes and nitrogenous excrements during vermicomposting which consequently cause the C/N ratio to decrease even further. Hence, this fully confirmed the ability of *Eudrilus eugeniae* in a faster breakdown and mineralization rates of organic material. A C/N ratio of <20 is suggestive of an advanced degree of organic matter stabilization and a level of acceptable maturity of a biodegradable substrate (Tumuhairwe et al., 2009), while a ratio of ≤ 15 is preferred for the application of composts in agronomy (Deka et al., 2011). Consequently, in this study, a high level of organic matter stabilization and an acceptable maturity were achieved in all the vermicomposted products generated from organic MSW (VS4, VS5 and VS6) but in only two of the composts from MSW (CS1 and CS2).

3.2. FT-IR spectroscopy

Infrared spectroscopy was used to identify the functional groups present in the MSW composts and vermicomposts. FT-IR spectra of the three types of compost and vermicomposts are given in Fig. A.1a–c (Supplementary material). The FT-IR spectra of compost, CS1 and vermicompost, VS4 derived from food waste is shown in Fig. A.1a. The common predominant peaks observed between 3388 and 3058 cm^{-1} marked the presence of phenols, aromatic, polysaccharides and saturated aliphatic species in CS1 and VS4 (Wang et al., 2013; El Ouaquodi et al., 2015). Phenols, alcohols and primary and secondary amines associated with O–H and N–H stretching vibrations respectively were clearly demarcated by the broad but small absorption bands between 3388 and 3245 cm^{-1} in both samples. Amide groups and alkenes were identified by the peaks between 3188 and 3126 cm^{-1} in CS1 whilst these peaks were not conspicuous in VS4 (Reusch, 2013). O–H stretching vibrations caused by carboxylic acids were accounted by the bands between 3058 and 2898 cm^{-1} in CS1 (El Fels et al., 2014). Aliphatic methylene groups were also detected between 2941 and 2892 cm^{-1} in both compost and vermicompost samples, confirming the presence of alkanes. Stronger but small varying peaks were observed between 2181 and 1707 cm^{-1} in CS1 corresponding to asymmetrical alkyne groups due to $\text{C}\equiv\text{C}$ stretching vibrations (Reusch, 2013). The shoulder at 1707 cm^{-1} and 1639 cm^{-1} in both CS1 and VS4 indicated the formation of ketones, aldehydes and carboxylic acid derivatives in the treated food waste due to the $\text{C}=\text{O}$ stretching vibrations (Droussi et al., 2009; El Fels

et al., 2014). The peak at 1639 cm^{-1} also corresponded to amide I group type (Tandy et al., 2010). Aromatic components in CS1 and VS4 were further detected via the peaks at 1472 and 1442 cm^{-1} caused by $\text{C}=\text{C}$ stretching vibrations (Droussi et al., 2009). $\text{C}-\text{O}$ stretching vibrations between 1054 and 1003 cm^{-1} demonstrated possible characteristics of primary alcohols, polysaccharides, aromatic ethers and esters in both treated food waste samples (Droussi et al., 2009; Ravindran and Sekaran, 2010; Wang et al., 2013; Reusch, 2013; Zhang et al., 2014; El Fels et al., 2014). Traces of alkyl halides and polysulfide groups were noted by the small varying peaks between 672 and 456 cm^{-1} in the compost and vermicompost samples from food waste (Reusch, 2013) although high band intensities were noted in VS4. The main functional groups present in CS1 and VS4 were comparable. Yet, major differences between the spectra of CS1 and VS4 lie in the variations in intensity of the absorption peaks especially as from 1054 cm^{-1} (Lim and Wu, 2015). VS4 showed more intense and stronger peaks compared to the flattened ones exhibited by CS1 between 3388 and 3245 cm^{-1} . A severe drop in phenolic content of CS1 accounted for this discrepancy (Hussain et al., 2016; Khan et al., 2016). The shortening in peak intensities in VS4 between 2892 and 1707 cm^{-1} was explained by the progressive alteration of polysaccharides (Lim and Wu, 2015) and degradation of complex lignocellulose components caused by enzymatic actions of worms during vermicomposting compared to traditional composting (Hussain et al., 2016). No peaks were detected between 1500 and 1600 cm^{-1} in any sample proving that both composting and vermicomposting caused degradation of lignocellulosic components (Hussain et al., 2016).

Fig. A.1b compares the FT-IR spectra of compost, CS2 and vermicompost, VS5 obtained from paper waste. The absorption band at 3299 cm^{-1} and 3269 cm^{-1} in CS2 and VS5 corresponded to O–H stretching vibrations caused by phenolic components and alcohols in the treated paper waste (El Ouaquodi et al., 2015; Hussain et al., 2016). The notable peak at 2918 cm^{-1} was ascribed to C–H stretching vibrations based on aliphatic methylene groups (Tandy et al., 2010; Wang et al., 2013; Zhang et al., 2014). The peak at 2639 cm^{-1} in CS2 was attributed to O–H stretching vibrations due to carboxylic acids confirming the formation of weak acidic compounds in paper waste compost (El Fels et al., 2014). Si components due to Si–H stretching vibrations were detected in both CS2 and VS5 samples between 2329 and 2174 cm^{-1} (Reusch, 2013; Zhang et al., 2014). Absorption at 2329 cm^{-1} was equally attributed to the $\text{C}\equiv\text{N}$ stretching vibrations in nitriles in CS2 and VS5 (Gupta and Garg, 2009). Carboxylic acid derivatives were identified

by the C=O stretching vibrations at 1705 cm^{-1} in both CS2 and VS5 while the absorption band at 1635 cm^{-1} was attributed to N–H bending vibrations in type amide I species (Tandy et al., 2010). The type amide II peptide bond due to N–H bending at 1598 cm^{-1} was visible in CS2 only (Li et al., 2011; El Ouaquodi et al., 2015). Aldehydes and ketones due to C=O stretching vibrations at 1434 cm^{-1} were observed in both samples (Wang et al., 2013). The small peak at 1325 cm^{-1} was accounted by C–N stretching vibrations caused by aromatic primary and secondary amines (Reusch, 2013). Prominent peaks between 1005 and 875 cm^{-1} were justified by C–O stretching vibrations in polysaccharides and carbonate species in the compost and vermicompost samples (Tandy et al., 2010). Smaller peaks between 875 and 524 cm^{-1} were accounted by traces of alkyl halides and polysulfide groups (Reusch, 2013). The disparity between the FT-IR spectra of CS2 and VS5 was evident based on the flatter and less intense peaks demonstrated by CS2 in comparison to VS5. The gap between CS2 and VS5 was wider than that between CS1 and VS4 as observed from Fig. A.1b. Shallower bands were observed for O–H, C=O and C–O stretching vibrations, at 3299 cm^{-1} , 1705 cm^{-1} and 1005 cm^{-1} respectively owing to the drop in phenolic components in paper waste compost (Hussain et al., 2016; Khan et al., 2016). Vermicompost from paper waste was dominated by phenols and polysaccharide species compared to CS2. The higher concentration of phenols in VS5 revealed that compost, CS2 was less toxic than VS5 (Hussain et al., 2016). Flattening bands between 2918 and 2639 cm^{-1} were assigned to the extensive decomposition of methylene groups in CS2 compared to VS5 (Lim and Wu, 2015). Peaks between 1500 and 1600 cm^{-1} were missing indicating complete degradation of lignocellulose in both compost and vermicompost (Hussain et al., 2016).

Variations in the composition of compost, CS3 and vermicompost, VS6 from yard waste can be compared from their FT-IR spectra from Fig. A.1c. Both CS3 and VS6 demonstrated overlapping peaks between 3341 and 3230 cm^{-1} caused by O–H stretching vibrations in phenols and alcohols. The small but noticeable peak at 2936 cm^{-1} in CS3 was accounted by C–H stretching vibrations in aliphatic methylene groups (Tandy et al., 2010; Wang et al., 2013; Zhang et al., 2014). The dense series of small peaks between 2357 and 2189 cm^{-1} was triggered by C=N stretching vibrations due to alkyne compounds in CS3 and VS6 respectively (Gupta and Garg, 2009; Reusch, 2013). The remarkable shoulder at 1632 and 1630 cm^{-1} indicated the presence of N–H bending vibrations in type amide I species and C=C stretching vibrations in aromatic compounds present in both treated yard waste samples (Tandy et al., 2010). The sharp and prominent absorption band between 1035 and 913 cm^{-1} was ascribed to C–O stretching vibrations caused by polysaccharides (Droussi et al., 2009; Li et al., 2011). Variations in peaks between 536 and 463 cm^{-1} advocated the presence of alkyl halides (Reusch, 2013). Unlike kitchen and paper wastes, the trend in FT-IR spectra of compost and vermicompost from yard waste was analogous. Most of the peaks were overlapping. The concentration of alcohols and phenols in yard waste compost and vermicompost were comparable. This implied that the toxicity effect of composting and vermicomposting yard waste was similar. VS6 was demarcated from CS3 as from 1632 cm^{-1} where shallower peaks were observed from the spectra of CS3. Degradation of lignocellulose was evident in both CS3 and VS6 based on the absence of peaks at 1500 and 1600 cm^{-1} (Hussain et al., 2016).

3.3. TG analysis

The normalized thermogravimetric (TG) and the derivative thermogravimetric (DTG) curves of the compost and vermicompost of food wastes, paper wastes and yard wastes are shown in

Fig. 2a–c. The first peak observed on the DTG curves in the temperature range 50 – $150\text{ }^{\circ}\text{C}$ for all the samples were due to the loss of moisture (Ravindran and Sekaran, 2010). Following dehydration, CS1 degraded in three stages with peaks around $185\text{ }^{\circ}\text{C}$, $276\text{ }^{\circ}\text{C}$ and $346\text{ }^{\circ}\text{C}$ while VS4 degraded in two stages with two distinct peaks on the DTG curve (Fig. 2a) around $305\text{ }^{\circ}\text{C}$ and $448\text{ }^{\circ}\text{C}$. The first peak for CS1 was mostly due to the decomposition of hemicelluloses occurring in this temperature range (170 – $210\text{ }^{\circ}\text{C}$) (Wu et al., 2011) and decarboxylation reactions of readily degradable materials (Pietro and Castaldi, 2004). The second peak in the temperature range of 210 – $300\text{ }^{\circ}\text{C}$ was due to the thermal breakdown of carbonaceous biomass where the degradation of carbohydrates and aliphatic compounds mostly take place (Fernandez et al., 2012). At higher temperatures (350 – $510\text{ }^{\circ}\text{C}$) as shown from Fig. 2a, the degradation of more stable and complex compounds such as lignin occurred (Baffi et al., 2007). The peaks of VS4 occurred at higher temperatures when compared to CS1 indicating that more thermal resistant components were present in the vermicompost due to increasing molar complexity and degree of aromaticity (Smidt and Lechner, 2005). Also, the intensity of the peaks for VS4 was much lower when compared to CS1 showing a slower rate of weight loss. The TG curve showed a residual mass of 45% from the thermal degradation of CS1 while the residual mass of VS4 was 53% indicating that the food waste vermicompost was more stable. The thermal decomposition of both CS2 and VS5 occurred in two stages in the temperature range of 195 – $395\text{ }^{\circ}\text{C}$ and 395 – $510\text{ }^{\circ}\text{C}$ (Fig. 2b). The residual mass after degradation was slightly higher for VS5 (61%) when compared to CS2 (59%) showing that a more stable product is formed from vermicomposting. Similar observations were made from the compost and vermicompost of yard waste where the residual mass of CS3 was 48% while that of VS6 was 71% (Fig. 2c), depicting a much higher mass loss occurred in CS3. Furthermore, the intensity of the peaks for VS6 was much lower and occurred at higher temperatures, thereby indicating a much stable product of the vermicomposted yard waste. Hence from thermogravimetric analysis of the three sets of organic MSW components, it can be deduced that vermicomposting process produced a more stabilized product as compared to normal composting. These results indicate that net mineralization have occurred during vermicomposting (Deka et al., 2011).

3.4. DSC analysis

Fig. 3a–c illustrated the DSC curves for all the three sets of vermicomposts derived from organic MSW with its paired controls. The DSC curve of CS1 in Fig. 3a pointed two obvious endothermic peaks at $83.8\text{ }^{\circ}\text{C}$ and $166.4\text{ }^{\circ}\text{C}$ respectively, which are characterized by the dehydration or the loss of peripheral polysaccharide chains and dehydroxylation reactions (Crittter and Airoidi, 2006). According to Provenzano et al. (2000), the sharp low-temperature endothermic peak at around $80\text{ }^{\circ}\text{C}$, as portrayed in Fig. 3a–c can be wielded as a measure to evaluate the maturity of composting residues. Following this statement, the low temperature endothermic peak is coincided to a higher maturity level of the compost materials. The second endothermic peak observed at $166.4\text{ }^{\circ}\text{C}$ coincided with the DTG peak for CS1 (Fig. 2a) and therefore indicates the energy required for the bond breaking during degradation of carbohydrates and aliphatic compounds. In contrast to CS1, VS4 revealed no endothermic peak at around $165\text{ }^{\circ}\text{C}$ (Fig. 3a) and appeared virtually flattened. Similarly, in this temperature range, no peak could be observed for VS4 on the DTG curve (Fig. 2a), thereby implying that for VS4 no degradation is taking place in that temperature range. Furthermore, this could be elucidated due to molecular reposition and re-orientation, possibly initiated by the loss of peptides structures and degradation of carbohydrates, aliphatic and other aromatics components (Gomez et al., 2007;

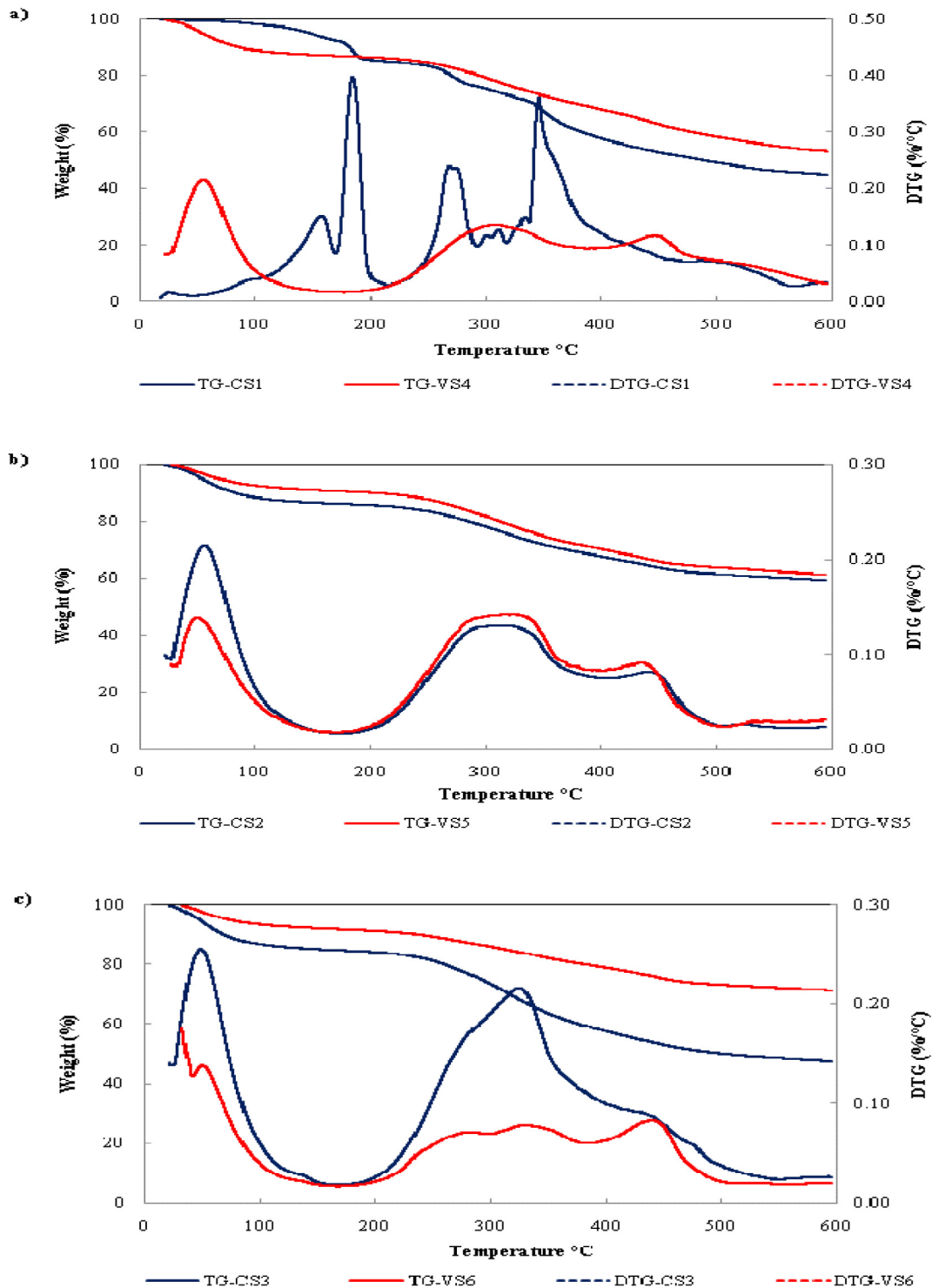


Fig. 2. TG and DTG curves of the compost and vermicompost from (a) food wastes (b) paper wastes and (c) yard wastes.

Fernandez et al., 2012). Similar to TG results (Fig. 2b), VS4 depicted an endothermic peak at a lower temperature (79.7 °C) when compared to CS1 which represents the energy absorbed for the dehydration process. Furthermore, the intensity of the endothermic peak has declined considerably which might be due to the inoculation of earthworms (Hussain et al., 2016). From Fig. 3b, CS2 yielded two minor distinct exothermic peaks, signifying that the net heat flow of all the samples has turned exothermic. The prime exothermic peak in the range 220–230 °C could be attributed mainly due

to the charring processes (Ball et al., 2004). The consequent exothermic peak in the range 250–300 °C could be justified from the oxidation, polycondensation and dissociation of the higher molecular weights complex aromatic structures; including both lignin and polyphenols (Pietro and Castaldi, 2004). These findings corroborate the results of the FTIR and TG analyses explained earlier. However, exceptionally as viewed from Fig. 3b, the endotherm maxima for VS5 has gained a meagre rise in the temperature level at 82.6 °C as compared to CS2 at 76.0 °C; probably owing to the

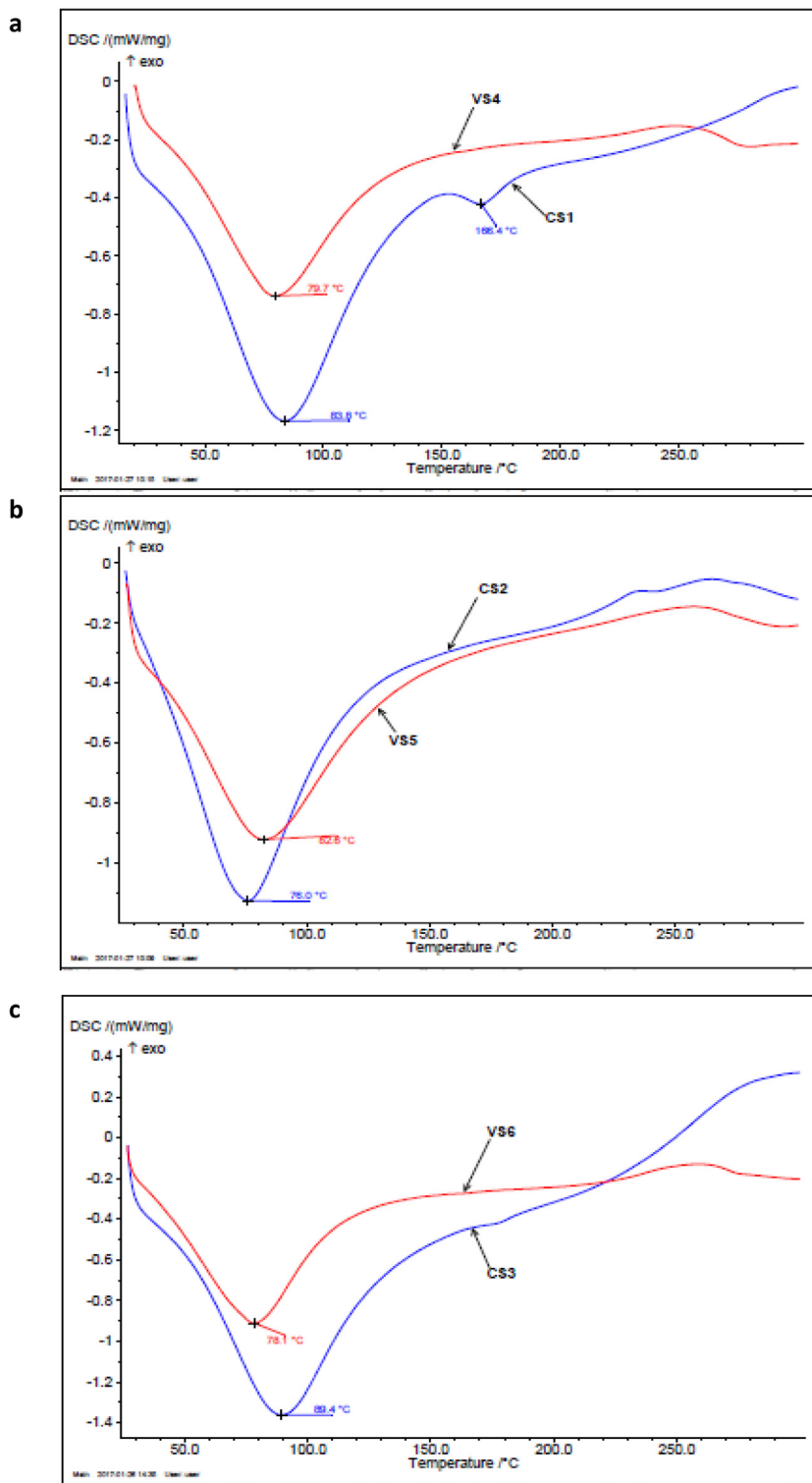


Fig. 3. DSC curves of the compost and vermicompost from (a) food wastes (b) paper wastes and (c) yard wastes.

stabilization and humification of the organic material during the vermicomposting process (Ali et al., 2012). The underlying principle was that the relative intensity of this endotherm is corroborated to the extent of humification of the paper waste composts which attenuated with elevating composting time, particularly during the maturity stage (Droussi et al., 2009). An endothermic peak at 89.4 °C was observed for CS3 whilst VS6 has shifted towards a temperature fall with an endothermic peak of 78.1 °C

(Fig. 3c) and this sharp low-temperature endothermic peak in VS6 could denote greater maturity as compared to CS3. As differentiated from all the compost DSC curves (CS1, CS2 and CS3) to its respective vermicompost DSC curves (VS4, VS5 and VS6), it could be discerned that all the peaks for vermicompost samples were generally less shallow with an upward shift from its corresponding compost samples. Furthermore, as illustrated in the VS4, VS5 and VS6 trends, there was the absence of any notable peak in the high

temperature range (250–300 °C); further concluding that the process of vermicomposting has remarkably degraded the complex organics in comparison to its respective paired compost samples.

3.5. SEM analysis

Fig. A.2a–f (Supplementary material) presented the micrographs of the three types of MSW vermicompost samples and their corresponding composts. Fig. A.2a revealed that CS1 (compost derived from food waste) was mostly compacted and firmly bounded by chemical bonds. In contrast, as seen in Fig. A.2b, the micrographs of food waste vermicompost VS4 was mostly flaky and disintegrated in nature. The tightly-packed microstructure of CS1 roughly corresponded with earlier finding made by Zhang et al. (2014) on composting of sewage sludge. From Fig. A.2a and b, these two SEM micrographs revealed that the final vermicomposting products exhibited a distinct physical appearance than composts and similar observations were reported for the other two vermicompost samples (VS4, VS6) compared with its respective compost samples (CS2, CS3). This observation somewhat correspond with the few recent research made by others authors (Lim and Wu, 2015; Hussain et al., 2016) on SEM analysis of vermicompost generated from other organic wastes but compared with the initial substrates. The micrographs of CS2 and CS3 (compost derived from paper waste and yard waste) (Fig. A.2c and e) showed that the compost had a packed fluffy and floc like structure while VS4 and VS6 (Fig. A.2d and f) are scattered and in much smaller fragments which might be due to the inoculation of earthworms *Eudrilus eugeniae* during the vermicomposting experiments. VS4, VS5 and VS6 were finer in texture since they were initiated from the disintegration and ingestion of organic MSW in the earthworm digestive tract, most particularly in the gizzard. Earthworms' activity has effectively degraded the long composite chains of MSW substrates into much tiny particle matter which has increased its value in soil applications as compared to traditional compost. As reported earlier, earthworms have the ability to grind a feed mixture they ingest by means of their muscular gizzard (Ali et al., 2015) resulting additional fragmentation by enzymatic and enteric microbial movements, numerous species of hydrolytic bacteria through the way of its transit in the earthworm gut (Arancon et al., 2005). This clearly facilitated an enhanced decomposition of the organic MSW which is revealed in the SEM images. From the SEM micrographs of the three sets of organic MSW components, it can be observed that vermicomposts (VS4, VS5, and VS6) were greatly connected by earthworm biomass substantiating the role of *Eudrilus eugeniae* in the examined MSW decomposition. Thus, it can be deduced that at the end of the vermicomposting, the morphological differences clearly depicted a higher maturity of the resulted MSW vermicomposts which was accomplished in the company of earthworms as compared to MSW composts.

4. Conclusions

FT-IR spectra demonstrated that vermicompost exhibited a greater reduction in readily degradable materials in contrast to composts. From the TG/DTG curves, the residual mass after thermal degradation was found to be slightly higher for vermicomposts than composts, depicting a more stable product. DSC curves revealed that there was an intense degradation of complex and larger biomolecules to simpler compounds in vermicompost compared to compost. SEM micrographs revealed that vermicompost reflected a flakier and disintegrated matrix than compost. Results showed that these analyses are reliable for a clear comparative elucidation between composts and vermicomposts in terms of stability and maturity indexes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2017.03.161>.

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