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Characterisation of dissolved organic matter extracted from the bio-oxidative phase of co-composting of biogas residues and livestock manure using spectroscopic techniques

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ABSTRACT

The composition of composting substrate significantly influences the composting process. To evaluate the effect of biogas residue content of initial composting mixture on the composting efficiency, co-composting processes of biogas residues and livestock manure (BRLM) were performed in terms of weight fractions of biogas residues (T1: 30%, T2: 40%, T3: 50% and T4: 60%). The dissolved organic matter (DOM) transformation was characterised. Fractionation of DOM, FTIR, UV–vis and fluorescence spectra indicated that the degradation efficiency of alcohols, ether and polysaccharides, and molecular weight, aromaticity and polycondensation degree of composts were in the order T3 > T2 > T1 > T4. Parallel factor analysis also showed that the content of humic-like substances was in the same order. Hierarchical cluster analysis showed that humified and stabilised degree of compost was optimal when the weight fraction of biogas residues was 40–50%. Bacterial profiles implied that biogas residue content of composting substrate significantly influenced bacterial dynamics. Bacteria were mainly active in the degradation of easily biodegradable organic matter and lignin. The abundance of bacteria involved in the degradation of easily biodegradable organic matter and lignin in the course of composting was closely related to composting efficiency and humification degree of compost.

Introduction

At present, with the rapid development of biogas engineering in China, there is an urgent need to dispose of a large amount of biogas residues from anaerobic digestion. In addition, the amount of animal manure is increasing because of the swift development of livestock farming. For example, the annual yield of animal manure in China is over 3 billion tons (Duan et al., 2012). Therefore, biogas residues and livestock manure have become two of the most important sources of agricultural pollution. Traditionally, biogas residues are often utilised directly as organic fertiliser (Yuan et al., 2011), which could result in the addition of hormones, chemical pesticides and potential ammonia oxidation-inhibiting substances, which are not conducive to plant growth. Livestock manure being used as the co-substrate for biogas residues composting can not only balance the C/N ratio of initial composting materials but also provide microbial biomass and a large amount of easily degradable organic matter (Creamer et al., 2010). More importantly, the negative influence of traditional biogas residue land utilisation on the soil could be eliminated or mitigated via composting (Singh and Kalamdhad, 2012, 2013; Ho et al., 2013).

Composting is a process involving continuous mineralisation and humification of organic matter (Gea et al., 2007). A typical composting process includes two general stages: the bio-oxidative phase and the following maturation phase. The former also consists of a mesophilic stage, a thermophilic stage and a falling-temperature stage (Yu et al., 2007). The rapid degradation of organic matter and reduction of volume and weight of compost piles are observed during the bio-oxidative phase of composting (BPC). This fact is convenient for the management of composting

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plants when considering the cost and the environmental impacts of composting. Therefore, research on organic matter dynamics during the BPC is important for shortening composting time and reducing the covering area of composting pile, thereby reducing the composting cost and environmental pollution.

As a highly active component, the characteristics of dissolved organic matter (DOM) and its transformations could reflect the composting process and the humification degree of organic matter. Extensive research has been conducted to explore the chemical structure and molecular weight changes of DOM during composting (Said-Pullicino et al., 2007; Wang et al., 2013). The application of spectroscopic methods, especially excitation-emission matrix (EEM), has become increasingly common (Tang et al., 2011; Wan et al., 2012). EEM spectra coupled with fluorescence regional integration (FRI) is often used to quantitatively analyse DOM (Tian et al., 2012; Lv et al., 2013). However, FRI cannot essentially solve the problem of overlap among the fluorescence peaks. Parallel factor analysis (PARAFAC) can decompose the three-way data into individual fluorescence components and quantitatively analyse DOM notably well because of its scientific nature (Yu et al., 2010; He et al., 2013a). However, the available information on DOM during the bio-oxidative phase of biogas residues and livestock manure co-composting is still limited, and biogas residue composting efficiency is also rarely reported.

The objectives of this study were to explore the dynamics of DOM during the bio-oxidative phase of biogas residues and livestock manure co-composting by spectroscopic techniques coupled with PARAFAC and to evaluate the effect of biogas residue content of initial composting mixture on the composting efficiency.

Materials and methods

Preparation of composting materials

Pig manure (PM) and chicken manure (CM) were collected from a pig farm and a chicken farm, respectively, in Hebei Province, China. After scraping off the hog-hair and feathers, the samples were collected, transported immediately to the laboratory and stored in a refrigerator at 4 °C until being used (less than 15 days). Biogas residues were collected from a farm in Beijing. It was pretreated by screening out the stones. Some characteristics of biogas residues and livestock manure (BRLM) are shown in Table 1.

Composting set-up and sampling

Four composting experiments with different biogas residue content (shown in Supplementary material (Table S1)) were conducted using aerobic composting reactors with the volume of 34 l. The basic characteristics of BRLM were as follows: C/N ratio, 21 to 26; water content, approximately 60% and pH value, 7.7 to 7.8. The oxygen was supplemented by ventilation (0.5 l kg^{-1} h^{-1}).

Compost samples were collected at different points from the top to the bottom of the piles after 0, 6, 14 and 30 days to follow the evolution of the DOM fraction. The sample was dried at 65 °C, ground and sieved to <1 mm for DOM extraction and parameter analysis. The measurements of physico-chemical parameters, germination index (GI) and spectra were performed 3 times per sample.

Table 1
Characteristics of the composting substrates.

Parameters	Pig manure	Chicken manure	Biogas residues
pH (1:10)	8.05 ± 0.19	7.82 ± 0.15	7.58 ± 0.11
Moisture content (%)	71.23 ± 7.36	73.42 ± 7.54	82.45 ± 8.13
Organic matter (%, d.m.)	80.90 ± 3.11	45.30 ± 1.57	35.70 ± 1.34
TN (g/kg, d.m.[a])	33.69 ± 4.23	27.88 ± 3.27	13.12 ± 2.31
TP (g/kg, d.m.)	35.56 ± 3.21	18.57 ± 1.55	15.03 ± 1.63
TK (g/kg, d.m.)	16.16 ± 0.87	11.39 ± 0.72	4.18 ± 0.46
C/N ratio	25.30 ± 1.29	9.10 ± 0.88	31.40 ± 1.43

[a] d.m. – dry matter.

Physico-chemical analysis and seed germination test

Temperature was determined online by temperature probes that were equipped with an aerobic composting reactor. The aqueous extracts (solid to water ratio of 1:10, w/v) of composting samples were prepared for measuring pH, ammonium–N and GI. The pH measurement was conducted using a Mettler Toledo S20K pH meter (Mettler Toledo Instruments, Shanghai, China). Ammonium–N was determined using Nessler's reagent spectrophotometry. GI was measured according to Said-Pullicino et al. (2007).

Extraction of DOM

The compost samples were extracted with distilled water (solid to water ratio of 1:10, w/v) for 24 h in a horizontal shaker at room temperature. The suspensions were then centrifuged at 10,000 rpm for 10 min, filtered through a 0.45-μm membrane filter and freeze-dried. Prior to UV–vis and fluorescence analysis, the dissolved organic carbon (DOC) of all the samples was measured with a multi N/C 2100 TOC/TN analyser (Analytikjena, Germany). The DOC concentrations of all the samples were standardised to make them comparable to each other and avoid inner filter effects for UV-absorbance and fluorescence analysis.

Fractionation of DOM

A tangential flow filtration system equipped with membrane packages of 65 Da, 1 kDa, and 5 kDa (Pall Corporation) was used to separate fractions of MW < 65 Da, 65 Da < MW < 1 kDa, 1 kDa < MW < 5 kDa, and MW > 5 kDa. The molecular weight (MW) fractions of DOM (C, mg kg^{-1}) were measured with a multi N/C 2100 TOC/TN analyser (Analytikjena, Germany).

Spectral analysis of DOM

FTIR spectra

The FTIR spectra were measured using a Nexus 670 FTIR spectrophotometer (Nicolet instrumental, USA). KBr pellets were obtained by pressing a mixture of 1 mg of freeze-dried DOM and 100 mg of dried spectrometry grade KBr under 10,000 kg cm^{-2} for 2 min. The spectra were recorded in the range of 4000–400 cm^{-1} with a 2 cm^{-1} resolution, and 64 scans were conducted on each sample

UV–vis spectra

UV–vis spectra were obtained with a UNICO 4802 UV–vis double beam spectrophotometer (UNICO, Shanghai, China) at a wavelength range of 200–400 nm. The specific ultraviolet absorbance at 254 nm ($SUVA_{254}$) and 280 nm ($SUVA_{280}$) was calculated as the absorbance divided by the DOC concentration. The ratios of the absorbance at 250 and 365 nm, E_{250}/E_{365}, and that at 253 and 203 nm, E_{253}/E_{203}, were also calculated.

Fluorescence spectra

Fluorescence spectra were obtained using an F-7000 fluorescence spectrophotometer (Hitachi, Tokyo, Japan). The slit widths for the excitation and emission monochromators were set at 10 nm. Synchronous-scan excitation spectra were obtained at a scan speed