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Characterization of dissolved organic matter from biogas residue composting using spectroscopic techniques

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ABSTRACT

Dissolved organic matter (DOM) extracted from composting of biogas residue was characterized using spectroscopic techniques. Spectral parameters, specific UV absorbance at 254 ($SUVA_{254}$), ratios of spectral slopes (S_R), and humification index (HIX) were used to assess the structural characteristics of the DOM. During composting, the UV absorbance at 254 increased as the relatively resistant aromatic fraction was released and the DOM molecular weight increased with the degree of humification. Fluorescence excitation-emission matrix (EEM) spectra with regional integration analysis (FRI) and accumulative fluorescence emission (AFE) combined with second derivative spectroscopy were used to assess the evolution of the DOM and evaluate the production of resistant humic-like substances during composting. Second derivative spectroscopy showed that microbial-derived humic-like substance A2 was easily degraded during composting. Two-dimensional correlation spectroscopy (2D-COS) combined with Fourier-transform infrared (FTIR) spectroscopy determined the preferential change sequence of the functional groups was 2000–2300 (C≡C or C═N) → 1288 cm^{-1} (amide III) at *x*1 and 2935 (aliphatic groups) → 1420 (carboxylic groups) → 3100–3400 (hydroxyl groups) → 1660 cm^{-1} (aromatic C═C) at *x*2, suggesting that functional groups of C≡C or C═N, and amide III can be degraded preferentially, and aromatic C═C groups were difficultly degraded. The present study showed spectroscopic techniques are valuable tools for assessing composting of biogas residues.

1. Introduction

Organic wastes, such as livestock manures and crop residues, which might otherwise release methane into the atmosphere can be converted into biogas. However, livestock manure has a relatively low energy content and farmers may be inclined to supplement it with farm food waste that would otherwise be sent to a landfill or composted (Tranter et al., 2011). Therefore, there is a clear need for the development of methods that allow utilization of these types of biowaste. Biogas technology is very attractive due to allowing utilization of certain biomass types for renewable energy (Yadvika et al., 2004). Anaerobic digestion has long been used to produce energy in biogas form while concurrently stabilizing waste organic matter (Leite et al., 2016). Anaerobic digestion of organic waste has significant potential for reducing global warming and climate change, as it promotes cycling of nutrient resources through nutrient-rich end products (i.e., biogas residues) and is an alternative to the energy-demanding production of mineral fertilizer (Clemens et al., 2006; Arthurson, 2009; Naroznova et al., 2016). Biogas residues as fertilizers are effective at conserving soil fertility, improving soil structure and humus balance, and promoting closure of natural nutrient and energy cycles (Insam et al., 2015; Coban et al., 2016). However, the quality of biogas residues need to be improved and proven to be efficient plant nutrient sources before being sold as crop fertilizers (Abdullahi et al., 2008).

Composting is an important method of treating solid waste (He et al., 2011; Awasthi et al., 2016; Meng et al., 2017), which can reduce waste volume and weight by approximately 50% and generate stable products (Fialho et al., 2010). Composting can improve the quality of biogas residues and the formation of stable and mature products. The use of unstabilized organic residues may inhibit plant growth and adversely affect the soil environment (Odlare et al., 2008). Composting implies the formation of humic-like substances by microorganisms with metabolisms that predominantly act in the water-soluble phase (Bernal et al., 2009).

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Water-extractable dissolved organic matter (DOM) is a very active component of biogas residues and plays a significant role in the migration of organic and inorganic pollutants into the environment (He et al., 2014; Yuan et al., 2015). Microbial decomposition is a major process that alters DOM characteristics and activity. Microbial transformation of DOM results in enrichment of aromatic carbon content and/or aliphatic components and, thus, a higher molecular weight (Chen et al., 2014).

It is difficult to distinguish between formation and accumulation of DOM over time, due to the fact that change in mass or volume of the system is not constant. However, the relative content of fluorescent components in DOM can be identified according to the changes in fluorescence intensity. Various spectroscopic techniques, such as Fourier-transform infrared (FTIR), ultraviolet–visible (UV–Vis), and fluorescence spectroscopy, have been used to explore DOM characteristics and activity. Fluorescence excitation-emission matrix (EEM) is useful for characterizing DOM from a range of environments. However, the traditional "peak-picking" technique is problematic when interpreting the multi-dimensional fluorescence EEM datasets due to overlap of fluorescence peaks (Yamashita et al., 2010). Accumulative fluorescence emission (AFE) spectroscopy analysis of fluorescence EEM spectra yields narrow and sharp spectra compared to conventional fluorescence emission spectroscopy and has been used to monitor DOM evolution (Yu et al., 2013). However, the selectivity of this method is restricted by extensive spectral overlap. Derivatives can amplify narrow bands and prevent broad bands and AFE can thereby reduce extensive spectroscopic overlap and neutralize matrix interference.

Recently, two-dimensional correlation spectroscopy (2D-COS) has been widely used to overcome the peak-overlap problem and enhance spectral resolution by extending peaks along a second dimension (Xu et al., 2013; Guo et al., 2017). In addition, 2D-COS allows easy identification of the sequential order of any subtle spectral changes arising from external perturbations (e.g., pressure, temperature, or concentration) over a second dimension (Noda and Ozaki, 2004). Therefore, 2D-COS combined with FTIR can be used to identify the sequential order of any subtle spectral changes arising from functional groups during composting. Although the characteristics and composition of DOM during composting have been widely studied, data specifically related to biogas residues remain scarce. Further studies on DOM compositional and structural changes due to microbial degradation during composting are still necessary. Therefore, the objectives of this study were (1) to investigate the spectroscopic and compositional characteristics of DOM extracted from composted biogas residue samples and (2) analyze DOM structural transformations during composting using 2D-COS combined with FTIR spectra.

2. Materials and methods

2.1. Experimental materials and sample collection

Biogas residues were collected from a biogas engineering using dry anaerobic fermentation process. Fermenting raw materials included a 1:2 mass ratio of straw and pig manure. The anaerobic fermentation experiments were carried out at a temperature of 35 °C and the entire process lasted 30 days. Biogas slurry was sprayed twice a day for a minimum of 30 min each through a dump pump to increase heat and mass transfer. Biogas residues were collected after 30 days of anaerobic fermentation and then composted.

Composting was carried out in a plastic drum (850 mm × 600 mm) with a cover. The stack was turned once a week and the cover opened twice a day for aeration. Composting was divided into active and curing periods. The active period lasted for 28 d, where the humidity was maintained above 50%. The curing period was also 28 d. Over the course of composting, the temperature increased from 30 to 66 °C, where the temperature began to decrease on day 28 and reached a constant ambient temperature after 42 d. Therefore, the entire composting process lasted approximately 42 d. Triplicate composting samples were collected at different timepoints from the top to the bottom of the piles after 0, 7, 14, 21, 28 and 42 d, although the samples were not differentiated by their levels within the piles. All samples were immediately placed into foam insulation boxes containing refrigerant for preservation and transferred to the laboratory on ice. Subsequently, all samples were freeze-dried using a lyophilizer (FD-1A-50, Bilon, China), ground, and then passed through 100-mesh sieves.

DOM extractions from compost samples were performed by mixing one part solid sample (20 g) with ten parts (200 ml) Milli Q water (w/v) and continuously shaking the mixture for 24 h at room temperature (He et al., 2011). Sodium azide was added to reduce the impact of microbial growth. The extracts were centrifuged for 10 min at 7000 rpm at 4 °C and then filtered through a 0.45-μm membrane. DOM concentrations were measured using a total organic carbon (TOC) analyzer (multi N/C 2100, Analytikjena, Germany). The TOC concentrations were 629.5, 531.5 431.5, 380.0, 321.5, and 312.0 mg/L, and the corresponding contents were 6.30, 5.32, 4.32, 3.80 3.22, and 3.12 mg/g at 0, 7, 14, 21, 28, and 42 d, respectively, indicating a decrease of DOM content during the composting.

2.2. Spectral analysis

FTIR spectra of pellets created by pressing a mixture of 1 mg of freeze-dried DOM and 300 mg of dried spectrometry-grade KBr under reduced pressure were obtained using a Nicolet Nexus FTIR spectrophotometer. The FTIR spectra were collected in the range 3600–400 cm^{-1} with a 2-cm^{-1} resolution.

Fluorescence EEM spectra were obtained by collecting at a series of excitation wavelengths between 220 and 450 nm at intervals of 5 nm and emission wavelengths between 280 and 550 nm at intervals of 5 nm using a fluorescence spectrofluorometer (F-7000, Hitachi, Japan) equipped with a 150-W Xenon arc lamp as the light source. The bandwidths for the excitation and emission modes were both set to 5 nm. Inner filter effects were corrected using a double-beam spectrophotometer (UV-1700, Shimadzu, Japan) with a 1-cm quartz cuvette with Milli Q water as a reference. TOC concentrations for all DOM samples were adjusted to 7 mg/L. Finally, the fluorescence signal of the Milli Q blank was subtracted and fluorescence was calibrated to the water Raman signal from excitation at 350 nm (Lawaetz and Stedmon, 2009).

2.3. Fluorescence EEM spectra with regional integration analysis

The EEM spectra of DOM from compost can be divided into five regions according to the fluorescence EEM spectra with regional integration (FRI) method described by Chen et al. (2003). The shorter excitation (<250 nm) and emission wavelengths (<380 nm) represent aromatic proteins, such as tyrosine and tryptophan (Regions I and II). The regions at the shorter excitation (<250 nm) and longer emission wavelengths (>380 nm) are related to fulvic acid-like substances (Region III). The regions located at the intermediate excitation (250–280 nm) and shorter emission wavelengths (<380 nm) are associated with soluble microbial byproducts (Region IV). The regions at the longer excitation (>280 nm) and emission wavelengths (>380 nm) correspond with humic acid-like organics (Region V). The integrations beneath the EEM spectra within the selected regions were calculated in this study. The cumulative volumes were normalized to relative EEM