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Relationship between anaerobic digestion of biodegradable solid waste and spectral characteristics of the derived liquid digestate

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HIGHLIGHTS

- Fluorescence peaks of tyrosine were appropriate for protein evaluation during AD.
- $SUVA_{254}$ and Ex/Em of 230/436 nm were suitable for evaluating humidification degree.
- E_4/E_6 and Ex/Em of 350/436 nm were unsuitable for evaluating humidification degree.
- Fluorescence peaks of tryptophan were inconsistent with dissolved protein content.

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ABSTRACT

The evolution of spectral properties during anaerobic digestion (AD) of 29 types of biodegradable solid waste was investigated to determine if spectral characteristics could be used for assessment of biological stabilization during AD. Biochemical methane potential tests were conducted and spectral indicators (including the ratio of ultraviolet–visible absorbance at 254 nm to dissolved organic carbon concentration ($SUVA_{254}$), the ratio of ultraviolet–visible absorbance measured at 465 nm and 665 nm (E_4/E_6), and the abundance of fluorescence peaks) were measured at different AD phases. Inter-relationship between organic degradation and spectral indicators were analyzed by principle component analysis. The results shows that from methane production phase to the end of methane production phase, $SUVA_{254}$ increased by 0.16–10.93 times, the abundance of fulvic acid-like compounds fluorescence peak increased by 0.01–0.54 times, the abundance of tyrosine fluorescence peak decreased by 0.03–0.64 times. Therefore, these indicators were useful to judge the course of mixed waste digestion.

1. Introduction

Global municipal solid wastes (MSWs) generation reached an estimated 1.3 billion tonnes per year in 2010 (Hoornweg and Bhada-Tat, 2012). MSWs contains many biodegradable components, but these components vary by region. For example, MSWs in the United States comprised 28% of paper, 14% of garden waste, and 15% of food waste in 2011 (US EPA, 2013). However, in Shanghai, the paper, garden waste, and food waste accounted for 11%, 1%, and 64% of the MSWs respectively in 2008–2009 (Shanghai Environmental Engineering Design and Science Academy, 2009). These components of MSWs are important organic sources of methane production through anaerobic digestion.

The residue of anaerobic digestion, called digestate, is usually used as soil amendments, and its biological stability is an important indicator of the environmental risk posed by the digestate (Senesi and Plaza, 2007). Several indicators have been proposed for assessment of the biological stability of MSWs and its derived materials, including the respirometric index, biomethane potential production, and the ratio of 5-day biological oxygen demand to chemical oxygen demand (BOD_5/COD) (Cossu et al., 2001). However, these parameters are limited by their high cost, long testing time, and low representativity in the presence of inhibiting substances. Comparatively, ultraviolet–visible (UV–Vis) absorption (Vieyra et al., 2009; Hunger and Weitkamp, 2001) and fluorescence spectra (Antunes and Da Silva, 2005) as assessment methods to represent biological stability and stabilization of dissolved organic materials (DOM) are rapid, highly sensitive and nondestructive. Nevertheless, few studies have been conducted to investigate the use of spectral indicators to evaluate biological stability and

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stabilization of anaerobic digestion, which were only limited to the leachate generated from anaerobic landfill for mixed MSWs (He et al., 2011; Lü et al., 2009).

The ratio of the UV–Vis absorbance measured at $\lambda = 254$ nm to the dissolved organic carbon (DOC) concentration ($SUVA_{254}$) and the ratio of the UV–Vis absorbance measured at $\lambda = 465$ nm to that measured at $\lambda = 665$ nm (E_4/E_6) are widely used to represent biological stability in UV–Vis absorption spectral indicators. $SUVA_{254}$ and E_4/E_6 have been reported to be particularly useful indicators for investigation of environmental samples (Weishaar et al., 2003; Chen et al., 1977), DOM of compost (Shao et al., 2009; Vieyra et al., 2009), and landfill leachate (He et al., 2011).

The excitation–emission matrix (EEM) spectra technology is increasingly being applied to represent biological stability and stabilization of environmental samples (Ishii and Boyer, 2012), DOM of compost (Yu et al., 2010), and investigation of anaerobic digestion of sludge (Luo et al., 2013), livestock manure (Wan et al., 2012), and mixed municipal solid waste (Ghita et al., 2013). Nevertheless, since the biochemical characteristics of various MSWs are quite different (Zheng et al., 2013), the DOM of various MSWs has different fluorescence spectra characteristics. For example, lignin is fluorescent, but polysaccharide is not; therefore, the fluorescence spectrum of lignocellulose waste is quite different from that of low lignocellulose content waste such as food waste. Accordingly, it is necessary to investigate whether EEM fluorescence spectra have consistent variation during anaerobic digestion processes of diverse biodegradable solid waste.

Most studies that have employed EEM spectra to probe the anaerobic digestion process have only used the "peak picking" technique (Ghita et al., 2013; Luo et al., 2013; Wan et al., 2012), which makes minimal use of the large quantity of data available in each EEM spectrum (Chen et al., 2003b). Comparatively, fluorescence regional integration (FRI) and parallel factor (PARAFAC) techniques (Shao et al., 2012) allow a more complete data mining than the traditional peak picking technique. Accordingly, combination of EEM with FRI and PARAFAC may provide deeper insight into the composition and behaviour of the DOM.

This study was conducted to investigate the relationship between spectral indicators and biological stabilization properties during anaerobic digestion of various biodegradable solid wastes with different biochemical compositions. To accomplish this, a biochemical methane potential (BMP) assay was utilized to simulate anaerobic digestion, which was then evaluated during the lag phase, methane production phase, end of methane production phase and excessive acidification phase. A combination of the absorption and fluorescence spectral properties, EEM–FRI/PARAFAC analysis and multivariate analysis was then used to compare the applicability of spectroscopy indicators to represent biological stability and stabilization during biodegradable solid waste anaerobic digestion.

2. Methods

2.1. Degradable material and inoculum

Based on the waste biochemical characteristics and production quantity, 29 types of precursor materials with the potential to be discarded as biodegradable solid waste were selected, including papers (newspaper, office paper, toilet paper), kitchen waste (fish bone, pork bone, lean pork, fat pork, soybean, potato, celery, lettuce), fruit waste (sugarcane residue, banana peel, orange peel, apple core and peel, watermelon peel, grapefruit peel), ligocellulosic materials (peanut shell, reed, the grass *Cynodon dactylon*, tea residue, bamboo leaf, bamboo branch, camphor tree leaf, camphor tree branch, metasequoia leaf, metasequoia branch, and cotton), and fabric. All collected materials were shredded to a size of less than 1 mm and then prepared for biochemical composition as described by Zheng et al. (2013).

The anaerobic inoculum was the digestate collected from an anaerobic digestion plant used to treat a mixture of sewage sludge and food waste. The inoculum had a total solids (TS) content of 23.8 ± 1.7 wt% and the volatile solids (VS) accounted for 81.9 ± 2.5 wt% of the TS.

2.2. Biochemical methane potential assay

Each 1 L glass bottle contained 100 g (wet weight) of inoculum, 400 g of nutrient medium, and 10 g (dry weight) of the tested biodegradable material, except for the reactors that contained toilet paper, orange peel and grapefruit peel. Only 5 g (dry weight) of the latter three materials were added because preliminary tests indicated that a higher inoculum-to-substrate ratio was required to avoid acidification. A blank reactor that contained only inoculum was also incubated to measure the background methane production. All experiments were carried out in duplicate. The nutrient medium, cultivation condition and gas measurement method described by Zheng et al. (2013) was employed.

The suspended mixtures in the bottles were obtained using a 5 ml syringe and then centrifuged for 10 min at 2000×*g*. Next, the supernatant was then passed through a 0.45-μm, microfiber filter, after which was referred to as the liquid digestate. Based on the methane production curve (Zheng et al., 2013), the lag phase of all materials except bamboo leaf was longer than 2 days; therefore, the liquid digestate of the lag phase was collected on the first day. When the methane concentration was higher than the carbon dioxide concentration, the liquid digestate of methane production phase was collected. When the methane production curve reached a plateau, the liquid digestate was collected at the end of the methane production phase. When anaerobic digestion reactors were failed due to excessive acidification, the liquid digestate of acidification phase was collected.

2.3. Analytical methods

2.3.1. UV–Vis spectra

UV–Vis spectroscopic measurements of the absorbance of liquid samples at 665, 465 and 254 nm were conducted using a UV-1800 UV–Vis spectrophotometer (Shimadzu, Kyoto, Japan) and 1-cm quartz cells. The unit of absorbance is m^{-1}. And DOC whose unit is mg L^{-1} was measured using a total organic carbon (TOC) analyzer (TOC-V CPN, Shimadzu, Japan). $SUVA_{254}$ values were determined by dividing the UV–Vis absorbance measured at $\lambda = 254$ nm by the DOC concentration and then reported in L mg^{-1} m^{-1} (Shao et al., 2009). E_4/E_6 values were determined by dividing the UV–Vis absorbance measured at $\lambda = 465$ nm by the UV–Vis absorbance measured at $\lambda = 665$ nm.

2.3.2. Fluorescence spectra

Prior to fluorescence spectroscopy analysis, the liquid digestate was diluted with 0.1 mol L^{-1} phosphate buffer to DOC < 10 mg L^{-1} to ensure that the maximum fluorescence signal was below the upper detection limit of the spectrometer and the disruption of inter- and intramolecular hydrogen bonds was eliminated (Ghita et al., 2013). The fluorescence EEM spectra of the liquid samples were recorded using a fluorescence spectrophotometer (Cary Eclipse, Varian, USA) in scan mode. To obtain fluorescence EEM, scanning emission (Em) spectral analysis was conducted from 250 to 600 nm at 2 nm increments by varying the excitation (Ex)