



Insight into the evolution, redox, and metal binding properties of dissolved organic matter from municipal solid wastes using two-dimensional correlation spectroscopy



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HIGHLIGHTS

- The change, redox and complexation property of dissolved organic matter were studied.
- Degradation was in the order of the aliphatic > protein > polysaccharide and lignin.
- Aromatic C and COO accounted for the oxidation ability of dissolved organic matter.
- O—C—O and COO were responsible for the Cu and Zn binding of dissolved organic matter.

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ABSTRACT

Two-dimensional correlation spectroscopy was employed to investigate the evolution, redox, and metal binding properties of dissolved organic matter (DOM) from municipal solid wastes (MSWs) during composting. The results showed that the DOM was degraded during composting in the order of aliphatic substances > proteinaceous compounds > cellulose, hemicellulose and lignin, while humic substances transformed during the process in the order of fulvic-like matter > humic-like substances > protein-like matter. The fulvic- and humic-like substances originated from lignin and polysaccharide-like substances with the function groups of CH₃, CCH₂, CCH, OCH₃, OCH, O—C—O, aromatic C, and COO, while the protein-like matter was derived from aliphatic and proteinaceous compounds with the functional groups of CCH₃ and N—C=O. The aromatic C and COO were responsible for the oxidation capacity of the MSW-derived DOM, while the O—C—O and COO accounted for the Cu and Zn binding capacity of the DOM.

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1. Introduction

Composting is a biological method for treating municipal solid wastes (MSWs), in which organic substances are degraded into inorganics and transformed into humus by microorganisms. Microbial metabolism occurs mainly in water-soluble phase during composting (Said-Pullicino et al., 2007), and dissolved organic matter (DOM) is an active organic fraction during the process (Shao et al., 2009; He et al., 2011). A study of the composition and

changes occurring in DOM can be useful for revealing the formation mechanism of humus and improving composting efficiency.

MSW-derived DOM is a heterogeneous substance that has a complicated composition and structure. Various chemical analysis techniques such as Fourier transform infrared (FTIR), nuclear magnetic resonance (NMR), and synchronous-scan fluorescence (SF) spectra have been used to investigate the composition and changes of DOM during composting (Zbytniewski and Buszewski, 2005; Amir et al., 2008; He et al., 2011). However, the results obtained from the traditional FTIR, NMR, or SF spectra methods may be incorrect because the individual spectral features of FTIR, NMR, or SF often overlap (Yu et al., 2011). Furthermore, using only FTIR, NMR or SF spectra to monitor DOM changes is insufficient because of the extreme heterogeneity of DOM constituents (Droussi et al., 2009; He et al., 2011; Yu et al., 2011). Integration of various spectra

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is the best way to monitor the changes of DOM during composting. However, an integrated analysis of these heterogeneous spectra is difficult and cannot be resolved using traditional methods (Yu et al., 2011).

The ascription of the peaks in the FTIR and NMR spectra is clear according to previous reports (Chefetz et al., 1998; Droussi et al., 2009; He et al., 2011). However, the moieties that are responsible for the peaks in the SF spectra have not been identified yet. Although previous reports have ascribed these peaks in the SF spectra to protein-, fulvic-, and humic-like substances (Hur et al., 2009; He et al., 2011), their detailed chemical composition and origin are still unclear.

Two-dimensional (2D) correlation spectroscopy is able to resolve the overlapped problem of different spectral signals of FTIR, NMR, or SF spectra by extending the signal over the second dimension (Noda, 1993). Furthermore, it allows one to easily probe the sequential order of spectral signal change in response to external perturbations such as pressure, temperature, and pH (Hur and Lee, 2011; Yu et al., 2011), which may be useful to investigate the response of MSW-derived DOM upon composting time. In addition, 2D heterospectral correlation spectroscopy is often used to investigate the covariation of two different spectra such as FTIR and SF (Yu et al., 2011). This approach may be a new way to identify the moieties that are responsible for the peaks in the SF spectra.

Heavy metals are often detected in MSWs, and their bioavailability and toxicity are related to their speciation (Leita and De Nobili, 1991; Smith, 2009). For instances, the heavy metals bound with humic substances exhibit a low bioavailability compared with the free metal ions, and hexavalent chromium shows a high toxicity with regard to trivalent chromium (He et al., 2014a). DOM can interact with heavy metals or adsorb hydrophilic organic pollutants due to the existence of O-, N-, and S-containing functional groups (Hur and Lee, 2011; Yu et al., 2012), which has an important influence on the bioavailability of the metals in MSWs (Xi et al., 2012). Furthermore, DOM can accept or donate electrons and act as an oxidant or reducing agent (Maurer et al., 2010; Gu et al., 2011), which change the valence state and toxicity of the metals such as Cr (He et al., 2014a). The redox ability of DOM is often quantized using electron acceptor capacity (EAC) and electron donor capacity (EDC) (Maurer et al., 2010; Yuan et al., 2012, 2013). Previous studies investigated the EAC, EDC, and metal binding ability of compost-derived DOM (Yuan et al., 2012, 2013; He et al., 2014a). However, the functional groups that are responsible for the redox and metal binding ability of MSW-derived DOM are still unclear and need further investigation. Therefore, the objectives of this study are to (1) investigate the evolution characteristics of MSW-derived DOM during composting using 2D correlation spectroscopy, (2) analyze the chemical composition and origin of the peaks in the SF spectra, and (3) identify the functional groups that are responsible for the redox and metal binding properties of MSW-derived DOM.

2. Materials and methods

2.1. Composting process and sampling

All composted MSWs were obtained from a composting plant located in Beijing, China. The composting process was discussed in our previous reports (He et al., 2011, 2014a) and briefly described as follows: The MSWs collected from Beijing were sorted manually and mechanically to remove metals, plastic, and glass, and organic residues were used for composting. More than 2 t of organic residues were used to compost each trapezoidal pile. The entire composting process lasted 51 d. The piles were turned every

2 d during the first 21 d and turned every 7 d in the next 30 d. The composted MSWs were collected after 0, 7, 14, 21 and 51 d of composting. To ensure a representative sample of the entire pile, triplicate composite samples (about 0.5 kg each) were collected at three different depths from the top to the bottom of the plies and then mixed together.

2.2. DOM extraction

According to Said-Pullicino et al. (2007), DOM was extracted from the composted MSWs with a solid-to-distilled water ratio of 1 (g):10 (mL). The obtained suspension was shaken for 24 h and then centrifuged at 10 000 rpm for 10 min. The supernatant was collected and filtered through a 0.45 μm membrane filter. The filtrates were divided into two parts. One part was freeze-dried for the FTIR and NMR spectral analysis, and the other was used to scan the SF spectra.

2.3. FTIR spectra

One gram of freeze-dried DOM sample was mixed with 300 g of dried spectrometry grade KBr, and the mixture was then pressed under 10 000 kPa for 2 min. The FTIR spectra were measured from 4000 to 400 cm^{-1} at 2 cm^{-1} resolution using a Nicolet Nexus FTIR spectrophotometer.

2.4. NMR spectra

Freeze-dried DOM samples were packed in 4 mm zirconia rotors, and solid-state CP/MAS ^{13}C NMR spectroscopy was measured using a Bruker model AV-300 spectrometer equipped with a standard 4 mm double bearing probe head. NMR spectra were obtained by applying the following parameters: 12 kHz rotor spin rate, 1 s recycle delay time, 2.4 μs pulse width time, and 2 ms contact time.

2.5. SF spectra

The dissolved organic carbon (DOC) concentrations of all DOM samples were measured using an Analytik Jena model Multi N/C 2100 TOC analyzer, and all of them were higher than 200.0 mg L^{-1} . To avoid inner filter effects for fluorescence spectra analysis, the DOC concentrations of all DOM samples were adjusted to 7.0 mg L^{-1} with deionized water. The SF spectra were obtained by scanning excitation wavelength from 250 to 595 nm with a constant offset of 30 nm using a Perkin-Elmer model LS50B fluorescence spectrophotometer.

2.6. 2D correlation spectroscopy

Composting time was used as external perturbation, and a set of time-dependent FTIR, NMR, or SF spectra were obtained. Then, 2D correlation spectroscopy was produced based on the time-dependent FTIR, NMR, or SF spectra using 2D Shige version 1.3 software (Kwansei-Gakuin University, Japan). The software was developed on the basis of the theory of generalized 2D correlation analysis, and the detailed algorithm adopted in the software was described by Noda and Ozaki (2004). In addition, 2D heterospectral correlation spectroscopy was conducted on the FTIR, NMR, and SF spectral data using 2D Shige version 1.3 software.

The 2D correlation spectroscopy is composed of synchronous and asynchronous spectroscopy. Two types of correlation peaks, i.e., auto-peak and cross-peak, can be observed at diagonal and off-diagonal positions, respectively, in the synchronous 2D correlation spectra. According to Noda's rule (Noda and Ozaki, 2004), the auto-peak is always positive, and its intensity represents the

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