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RESEARCH PAPER

Electron Transfer Capacities of Dissolved Organic Matter Derived from Swine Manure Based on Eletrochemical Method

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Abstract: Dissolved organic matter (DOM) is the most active fraction of compost organic matter. The presence of the redox-active functional groups in DOM allows it to act an electron shuttle to promote the electron transfer between microorganisms and terminal electron acceptors. In this study, the electron transfer capacities (ETCs) of compost DOM samples at eight different composting stages were determined by electrochemical method. 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) and Diquat dibro-mide monohydrate (DQ) were used to measured electron donating capacity (EDC) and electron accepting capacity (EAC) at working voltage 0.61 V/–0.49 V, respectively. The evolution characteristics of the chemical structures and components were analyzed by combining the three-dimensional fluorescence spectra, Fourier transform infrared (FTIR) spectra and elemental analysis. The results showed that the EDC of DOM increased from 16.850 μmol e^- (g C)$^{-1}$ to 22.077 μmol e^- (g C)$^{-1}$, The EAC decreased from 1.866 μmol e^- (g C)$^{-1}$ to 1.779 μmol e^- (g C)$^{-1}$. The results of three-dimensional fluorescence spectroscopy showed that the relative contents of humic-like and protein-like components gradually increased and decreased, respectively, during the composting process. The humuc-like components were the main contributor for the ETC of DOM. FTIR spectra showed that there was no significant change in the hydroxyl and carboxyl group contents of DOM during composting, suggesting no contribution of these function groups to the ETC of DOM. The elemental analysis showed that the content of oxygen in the DOM increased during the composting process, while the sulfur-containing group might be dominated contributor for its ETC.

Key Words: Composting; Dissolved organic matter; Electron transfer capacity; Three-dimensional fluorescence; Infrared spectroscopy

1 Introduction

In recent years, with the improvement of living standards in our country, the demand for meat products is increasing day by day, resulting in the continuous enlargement of the scale of livestock and poultry breeding. The recycling of organic waste from livestock and poultry farming has become a current concern[1]. Swine manure is a high-quality source of nutrients because it contains abundant organic matter and high nitrogen content and is susceptible to the use of microorganisms, but the improper disposal of swine manure may cause many environmental problems, such as the generation of large amounts of greenhouse gas, foul gas pollution, and pathogens diffusion, and even pollutes the water[2]. Composting is an

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effective way to recycle organic waste and is widely used to treat livestock and poultry excrement, producing valuable composted products while eliminating pollution.

The mostly reactions occur at the solid-liquid interface during composting, so dissolved organic matter (DOM) is the most active organic matter in the composting process. Therefore, the DOM evolution can reflect the process of composting conversion and composting stability[3]. The structure and composition of compost DOM is complex, which contains not only low molecular weight free amino acids, carbohydrates, and other substance but also a variety of high molecular weight components such as enzymes, polyphenols, humic acid and other compounds, so it is difficult to determine the DOM specific Chemical structure[4,5]. The main elements of DOM are C, H, O, N and S. The components of DOM in different components are significantly different[4]. In addition, DOM also contains a large number of highly active site functional groups with electron transfer ability, such as phenolic, hydroxyl, carboxyl, thiols and amides and others, so compost DOM has a redox ability[5–7].

Under anaerobic conditions, the redox capacity of DOM makes it available as the electron shuttle that facilitates the transfer of electrons between electron donors (microbes, hydrogen sulfide, etc.) and electron acceptors (iron minerals, contaminants). First of all, DOM can be regarded as the electron acceptor to accept electrons from the microorganisms themselves, then the reduced DOM can serve as the electron donor to transfer electrons to acceptor contaminants and reduce the environmental risk of pollutants. Some studies have shown that the DOM can not only promote the reduction of Cr(VI) and Fe(III) by electron shuttle but also enhance the degradation of nitrobenzene[8–11]. Therefore, it is necessary to study the effect of DOM structure and composition changes on the electron transfer capacity during composting of swine manure, and then understand the process of stabilization and detoxification of composting process, and also provide scientific support for the regulation and control of composting products with good environmental effects. However, the evolution of DOM electron transfer capacity in swine manure composting is rarely reported at present.

In this study, the electron donating capacity (EDC) and EAC of DOM were determined by electrochemical analysis with different mediators. The evolution of DOM composition was characterized by three-dimensional fluorescence spectroscopy, and based on the previous studies[5], DOM elemental analysis and infrared spectrometry were used to explore the changes of DOM structure and functional groups so as to investigate the effects of changes in chemical structure and composition of DOM on the evolution of electron transfer capacity in swine manure composting.

2 Experimental

2.1 Instruments and reagents

CHI-660e electrochemical workstation (Chenhua Company, China) and all electrode were purchased from Chenhua Company. TENSOR II Fourier transform infrared spectrometer (Bruker, Germany), Hitachi F-7000 Fluorescence Spectrometer (Hitachi, Japan), VARIO EL cube Elemental analyzer (Elementar, Germany), Analytik Jena Multi N/C 2100 TOC analyzer (Analytik Jena, Germany) were used in this study.

KBr(SP), NaH_2PO_4(AR), Na_2HPO_4(AR) and KCl(GR) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd, China. 2,2'-azino-bis(3-ethylbenzothiazoline-sulfonicacid) (ABTS, > 98%) was purchased from Tokyo Chemical Industry Co., Ltd, Japan. Diquat dibromide monohydrate (DQ, 99.5%) was purchased from the National Institute of Metrology, China. 0.45 μm filter membrane of 25 mm in diameter was purchased from Tianjin Jinteng Company, China. 0.05 μm alumina polishing powder was purchased from Shanghai Chuxi Industrial Co., Ltd., China.

2.2 Sample collection and DOM extraction

Swine manure sample was collected from Northwest A & F University, and the compost raw material was the mixture of swine manure and straw with the mixed ratio of 2:1. Forced ventilation was used as compost condition, and the compost weight was about 100 kg. A total of 8 stages of compost samples were respectively collected after composting for 1, 4, 8, 15, 22, 29, 36 and 43 days. The samples were taken by the frozen transport to Beijing, and stored at –20 ºC.

Extraction of DOM according to the method of reference[12]. Firstly, freeze-drying was performed at –54 ºC for 48 h to remove moisture from the compost sample. Secondly, the dried sample was ground in the mortar and sieved through the 100-mesh sieve to obtain sample powder. Next, the ultrapure water and the sample powder were mixed according to the ratio of 10 mL:1 g, and then shaken at speed of 250 rpm for 24 h in the shaker. The resulting mixture was centrifuged at 11000 rpm for 10 min at low temperature, and the supernatant liquid was retained. Finally, DOM of swine manure sample was obtained by supernatant through a 0.45-μm filter membrane. After the DOM was diluted by 100-fold with ultrapure water, the dissolved organic carbon (DOC) of DOM diluent was measured by Total organic carbon (TOC) analyzer, and DOC of DOM was calculated.

2.3 Electrochemical measurements

Electron transfer capacity (ETC) of compost sample DOM was determined by electrochemical measurements (Fig.1) according to the method from literatures[8,13]. The three-electrode system was used as the electrochemical reaction system, with Ag/AgCl electrode as reference electrode, platinum wire electrode as counter electrode, and a glassy