



Utilization of medical stone to improve the composition and quality of dissolved organic matter in composted pig manure

Quan Wang^a, Mukesh Kumar Awasthi^{a, b}, Junchao Zhao^a, Xiuna Ren^a, Meijing Wang^a, Ronghua Li^a, Zhen Wang^a, Zengqiang Zhang^{a, *}

^a College of Natural Resources and Environment, Northwest A&F University, Yangling 712100, PR China

^b Department of Biotechnology, Amicable Knowledge Solution University, Satna, India

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ABSTRACT

This research was conducted to evaluate the effect of medical stone (MS) on the dissolved organic matter (DOM) extracted from composted pig manure (PM). Five treatments with different MS amounts (0%, 2.5%, 5%, 7.5% and 10% of PM by dry weight) were mixed with the initial feedstock and composted for 60 days. DOM was extracted from the composted materials and characterized using spectroscopic techniques, including UV–visible, Fourier transform infrared (FTIR) and fluorescence spectroscopy. The results showed that the addition of MS improved the biodegradation of protein-like materials, ether, alcohols, and polysaccharides. Compared to the control, the ratios of FTIR spectra peaks ($1645\text{ cm}^{-1}/1407\text{ cm}^{-1}$, $1645\text{ cm}^{-1}/2930\text{ cm}^{-1}$, and $1645\text{ cm}^{-1}/1003\text{ cm}^{-1}$) in treatments in which MS was added were higher, and the peak ratio ($1645\text{ cm}^{-1}/1103\text{ cm}^{-1}$) was increased by 4.54%–10.22%. Adding MS could also increase the SUVA₂₅₄ and SUVA₂₈₀ values while decreasing the E₂₅₀/E₃₆₅ ratio, which indicates that the addition of MS increases aromaticity and molecular weight of the compost as well as humic-like compounds. Furthermore, the addition of MS improved the efficiency of the composting process and the rate of humification. The P_{in} of region V in the MS amended treatments (53.86%–56.66%) was higher than in the control (52.17%), and 10% MS addition yielded the highest value. Overall, the results show that the addition of 10% MS to PM is beneficial to the composting process.

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1. Introduction

Composting is widely accepted as an appropriate management technique for disposing of and recycling organic waste, such as sewage sludge, animal manure, food waste and municipal solid waste (Li et al., 2012; Zhang and Sun, 2015; Chan et al., 2016; Awasthi et al., 2017). Composting technology can reduce the volume and weight of the organic waste, and generate a stable and harmless product (compost), which can be used as a soil amendment or fertilizer (Bernal et al., 2009). However, conventional composting still presents several drawbacks, such as nitrogen loss, low composting efficiency and undesirable final product quality (Wang et al., 2016a). The use of unstabilized or immature compost will poison crops, inhibit seed germination and adversely affect the ecology (Huang et al., 2006). Therefore, improvement in

composting technology and compost maturity are both essential for enhancing the use of compost.

In recent years, the incorporation of mineral additives (e.g., biochar, zeolite, lime and medical stone) to improve the composting process, promote compost maturity, and accelerate the organic matter degradation, has been widely reported (Dias et al., 2010; Gabhane et al., 2012; Awasthi et al., 2016a; Wang et al., 2017). Turan (2008) and Villasenor et al. (2011) discovered that adding zeolite could reduce the salinity levels of compost and improve the quality of the final product. Dias et al. (2010) stated that co-composted poultry manure with wood biochar could promote the degradation of organic materials and the maturation of compost, which was in agreement with the results of Khan et al. (2014), who studied chicken manure composting. Moreover, some researchers found that adding a mixture of additives could also improve composting efficiency and promote OM humification (Zhang and Sun, 2015; Awasthi et al., 2016b). Overall, the addition of mineral additives could improve the porosity and microbial activity during composting, facilitate the organic matter transformation, and

* Corresponding author. College of Natural Resources and Environment, Northwest A&F University, Yangling, Shaanxi Province, 712100, PR China.

E-mail address: zhangzq58@126.com (Z. Zhang).

enhance the quality of the end product (Li et al., 2012; Chan et al., 2016; Awasthi et al., 2017).

Most of the biological activity in the composting process occurs in a water-soluble phase, and the variation of dissolved organic matter (DOM) could reflect the biochemical transformation of organic materials and the stabilization of compost products (He et al., 2013a; Wei et al., 2014). Additionally, DOM contains various kinds of oxygen-containing and aromatic functional compounds, which could interact with a number of inorganic and organic contaminants (Plaza et al., 2009). Thus, knowledge of the composition and structural characterization of DOM extracted from compost is very important for evaluating the quality and maturation of the final compost. Meanwhile, improving the composition and quality of dissolved organic matter is beneficial for the successful utilization of compost. To date, different type of spectroscopic techniques such as UV–visible, Fourier transform infrared (FTIR), and fluorescence spectroscopy, have been utilized to assess the composition, chemical structure and spectroscopic features of organic substances that extracted from the compost, such as humic acid, fulvic acid and DOM (Shao et al., 2009; He et al., 2011; Xi et al., 2012; Song et al., 2015). Furthermore, substantial previous research has indicated that integrating various spectroscopic methods (FTIR, UV–visible, and fluorescence) to characterize OM is better than using a single spectroscopic technique (Xi et al., 2012; Wei et al., 2014; Song et al., 2015). With the help of the spectroscopic techniques, some research has been conducted to explore the effect of biogas residue and microbial agent on chemical structure and molecular weight variations of DOM and fulvic acid (Xi et al., 2012; Song et al., 2015).

The use of medical stone, a novel mineral additive, has been applied to pig manure and sewage sludge composting to improve nitrogen conservation and OM degradation as well as enhancing the composting process (Wang et al., 2016b; Awasthi et al., 2018). However, the effect of adding MS on the variation of DOM generation during PM composting has not previously been reported. Therefore, the aims of this research are to investigate the structure and composition of DOM during PM composting when different amounts of MS are added. This research may supply important information regarding the application of mineral additives for organic waste composting.

2. Materials and methods

2.1. Materials and the composting process

The PM and sawdust used in this study were gathered from a local hogery and wood-processing plant in Yangling township, Shaanxi, China. The mineral additive (medical stone) was obtained from Shijiazhuang Jiacheng Building Materials Co. Ltd., China. Fresh PM and sawdust were mixed at a ratio of 2:1 (dry weight), and different dosages (0%, 2.5%, 5.0%, 7.5% and 10%) of MS were added into the initial feedstock on a dry weight of PM basis, and denoted as the control, T1, T2, T3 and T4, respectively. The moisture content, bulk density and C/N ratio of the initial mixtures were adjusted to 55–60%, 0.5 kg/L and ~35, respectively, according to the method of Bernal et al. (2009). The main chemical and physical characteristics of the raw materials are shown in our previous study (Wang et al., 2016b). After complete mixing, the compost mixtures were individually placed into 130-L PVC composters and later composted for 60 days. The specifications of the composting reactor and the operational details of the composting process are provided in our previous studies (Li et al., 2012; Wang et al., 2016a). Samples were collected from the initial mixture and the final compost products after different treatments, and later stored at -20°C prior to analysis.

2.2. Extraction of DOM

Samples for the determination of DOM were obtained as described by He et al. (2013b). Each sample was extracted with ultrapure water at the ratio of 10:1 and subsequently shaken for 24 h at room temperature. After centrifuging at 12000 rpm for 20 min, the suspensions were filtered through a $0.45\ \mu\text{m}$ membrane. The filtrate was later divided into two parts for further analysis; one aliquot was analyzed by UV–visible and fluorescence spectroscopy, while the other aliquot was freeze–dried and analyzed by FTIR spectroscopy.

2.3. FTIR spectra

The abovementioned DOM and dried KBr (spectrometry grade) were mixed at a ratio of 1:200 and later pressed into pellets according to the method of He et al. (2013a). The Nicolet 8700 FTIR spectrophotometer was used to detect the FTIR spectra over the range of 4000 to $400\ \text{cm}^{-1}$ with a resolution of $2\ \text{cm}^{-1}$; each sample was scanned 64 times, and ultrapure water was used as the reference beam blank.

2.4. UV–vis spectra

Before recording the UV–vis spectra and fluorescence spectra, the organic carbon of all DOM samples were adjusted to $7\ \text{mg/L}$ according to the method of He et al. (2011). A Shimadzu UV–1452 spectrophotometer was used to measure the UV–vis absorption spectra in the 220 – $600\ \text{nm}$ wavelength range. The absorbance at $254\ \text{nm}$ (SUVA_{254}) and $280\ \text{nm}$ (SUVA_{280}) and the ratio of the specific ultraviolet absorbance at $250\ \text{nm}$ and $365\ \text{nm}$ (E_{250}/E_{365}) were calculated according to the method of Song et al. (2015).

2.5. Fluorescence spectra

The fluorescence spectra were recorded using a Hitachi model F–4600 fluorescence spectrophotometer. The excitation and emission monochromators slit widths were $10\ \text{nm}$, and the scan speed was set to $1200\ \text{nm/min}$. Emission spectra were recorded over the 280 – $520\ \text{nm}$ range at a constant excitation wavelength of $254\ \text{nm}$. The ratio of the areas at 435 – $480\ \text{nm}$ and at 300 – $345\ \text{nm}$ were denoted as A_4/A_1 . Synchronous fluorescence spectra were detected over 250 – $600\ \text{nm}$ range using a constant offset of $\Delta\lambda = 30\ \text{nm}$. The ratio of areas between 250 and $308\ \text{nm}$, 308 – $363\ \text{nm}$ and 363 – $500\ \text{nm}$ were calculated as the percentages, and designated $A_{250-308}$, $A_{308-363}$ and $A_{360-500}$ respectively. Excitation–emission matrix (EEM) fluorescence spectra were detected over the ranges of 200 – $400\ \text{nm}$ (excitation wavelength) and 280 – $520\ \text{nm}$ (emission wavelength). A data interpolation was used to regulate the Rayleigh and Raman scatter (Bahram et al., 2006), and the fluorescence regional integration (FRI) method was used to evaluate the EEM spectra (Chen et al., 2003).

3. Results and discussion

3.1. FTIR spectra

The FTIR spectra of all samples contained similar peak locations (Fig. 1). The major absorption bands were characterized by (i) O–H stretching of phenols, carboxylic, and alcohols at $\sim 3400\ \text{cm}^{-1}$; (ii) C–H stretching vibrations of aliphatic structure at $\sim 2930\ \text{cm}^{-1}$; (iii) mainly C=C skeletal vibrations of aromatic rings at $\sim 1645\ \text{cm}^{-1}$; (iv) N–H deformation and C=N stretching of amides at $\sim 1570\ \text{cm}^{-1}$; (v) C–O asymmetrical stretching of carboxyl and symmetric stretching of the COO^- at $\sim 1407\ \text{cm}^{-1}$, (vi) C–O

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