Bioresource Technology 245 (2017) 300–308

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Comparison of biochar, zeolite and their mixture amendment for aiding organic matter transformation and nitrogen conservation during pig manure composting

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ARTICLE INFO

Keywords:
Composting
Pig manure
Ammonia
Nitrogen dioxide
Humification

ABSTRACT

The aim of this work was to compare the impact of biochar, zeolite and their mixture on nitrogen conservation and organic matter transformation during pig manure (PM) composting. Four treatments were set-up from PM mixed with wheat straw and then applied 10% biochar (B), 10% zeolite (Z) and 10% biochar + 10% zeolite (B + Z) into composting mixtures (dry weight basis), while treatment without additives applied used as control. Results indicated that adding B, Z and B + Z could obviously ($p < 0.05$) improve the organic matter degradation and decrease the nitrogen loss. And combined addition of B and Z further promoted the organic matter humification and reduced the heavy metals mobility. Meanwhile the highest mitigation of ammonia (63.40%) and nitrogen dioxide (78.13%) emissions was observed in B + Z added treatment. Comparison of organic matter transformation, nitrogen conservation and compost quality indicated that the combined use of biochar and zeolite could be more useful for PM composting.

1. Introduction

In China, the fast development of intensive pig production has generated large quantities of pig manure (PM) with relatively insufficient land for application (Li et al., 2012; Jiang et al., 2016b). Unsuitable management of PM would result in a series of environmental issues such as water and soil pollutions by excessive input of nutrients, immature organic materials and heavy metals (HMs) (Huang et al., 2006; Chen et al., 2010). Composting of PM has been widely accepted and one of the most eco-friendly approaches, which could transform the complex organic substrate into sanitary and stabilized end product, thus serving as organic fertilizer (Bernal et al., 2009; Li et al., 2012). However, adverse manifestation during the traditional composting process is the excessive ammonia (NH_3) emission and the low degree of organic matter transformation, which not only reduced the agronomic value of compost as a soil fertilizer or amendment, but also decreased the environmental benefits of composting (Huang et al., 2006; Yang et al., 2015; Awasthi et al., 2017a,b).

Recently, many practical approaches such as adjusting the physicochemical parameters (Huang et al., 2004; Dias et al., 2010), changing the aeration rate (Chowdhury et al., 2014; Yuan et al., 2016) and adding the different kinds (chemical, microbial and mineral, etc.) of additives (Gabhane et al., 2012; Jiang et al., 2015; Chan et al., 2016; Awasthi et al., 2017a,b) have been carried out to promote the composting process and reduce the adverse effect as mentioned above for composting. To date, the addition of the mineral additives to improve the composting efficiency, organic matter transformation, nitrogen conservation and greenhouse gases (GHGs) mitigation are increasingly attracted the interest of researchers (Chen et al., 2010; Li et al., 2012; Wang et al., 2016b; Zhang and Sun, 2017b). Among the all additives, biochar and zeolite were the most common amendments and have been widely used to improve the organic matter transformation and nitrogen conservation (Li et al., 2015; Chan et al., 2016; Awasthi et al., 2017a,b). For example, Chen et al. (2010) and Awasthi et al. (2016a) investigated that the amendment of biochar could improve nitrogen conservation and facilitate the organic matter degradation during the PM and sewage sludge (SS) composting. Dias et al. (2010) and Jindo et al. (2016) demonstrated that co-composting animal manure with biochar could promote the organic matter humification and promote the final compost quality. On the other hand, Zhang and Sun (2015) stated that adding the zeolite could obviously improve lignocellulose decomposition and increase the humic acid content during the green waste

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http://dx.doi.org/10.1016/j.biortech.2017.08.158
Received 22 July 2017; Received in revised form 23 August 2017; Accepted 25 August 2017
Available online 30 August 2017
0960-8524/

composting. Chan et al. (2016) indicated that zeolite could mitigate 25.02% NH_3 emission and accelerate the organic matter decomposition during food waste composting. Moreover, our early research also found that combined addition of biochar and zeolite could prominently lower the GHGs emission and improve the nitrogen conservation during SS composting (Awasthi et al., 2016c).

Consequently, the literatures above-cited indicated that adding the biochar, zeolite and their mixture could be an effective method to improve the composting process and reduce the secondary pollution. However, comparison of biochar, zeolite and their mixture amendments for improving the organic matter transformation and nitrogen conservation during the PM composting has not been well reported. Therefore, the purpose of this study was to compare the effect of biochar, zeolite and their mixture on organic matter transformation and nitrogen conservation as well as the quality of end product during PM composting.

2. Materials and methods

2.1. Composting material collection and processing

Fresh PM and wheat straw (WS) were collected from a local hoggery and farmland in Yangling town, Shaanxi, China. Biochar and zeolite were purchased from Yangling Yixing Biotechnology Co. Ltd., China and Zhejiang Shenshi Mining Industry Group Co., Ltd., China, respectively. Biochar were crushed into fine particles (2–5 mm), and mixed with zeolite and then added into composting mass as additives. WS was chopped to 1 cm and used to adjust the moisture content (~55–60%), C/N ratio (~25) and bulk density (~0.5 kg/L) of the initial compost mixtures (Bernal et al., 2009; Li et al., 2012). The selected physico-chemical characteristics of raw materials were presented in Table 1, and the Brunauer-Emmett-Teller (BET) surface area (5.99 $m^2 g^{-1}$), C (43.85 ± 2.42%), O (10.02 ± 0.08%) and H (2.16 ± 0.05%).

2.2. Composting system and experimental design

The composting experiment was done in 130-L polyvinyl chloride (PVC) reactors (100-L work volume) for 50 days, and the operational composting process and reactor dimension were already define in Wang et al. (2016a). Fresh PM and WS were mixed at 2:1 ratio (dry weight basis) and then combined with 10% biochar (B), 10% zeolite (Z) and 10% biochar + 10% zeolite (B + Z) on initial feed stock dry weight basis, respectively. Whereas, the treatment without additives was regarded as control for comparison purpose. The temperature of composts and ambient was monitored three times per day and then recorded the average value. After composting materials were mixed thoroughly, homogeneous samples of compost were taken on days 1, 8, 22, 36 and 50 during composting. The collected samples was divided into two parts; one part was stored at 4 °C till analysis, while the another part was air dried, grounded to pass through a 0.1 mm sieve and thoroughly mixed for further analysis.

Table 1
The physicochemical properties of raw materials used in this research.

Parameter	Pig manure	Wheat straw	Biochar	Zeolite
Moisture (%)	63.12 ± 1.10	6.45 ± 0.20	7.31 ± 0.21	0.60 ± 0.06
pH	8.00 ± 0.06	6.57 ± 0.14	10.80 ± 0.02	9.39 ± 0.03
EC (mS/cm)	5.41 ± 0.11	2.72 ± 0.26	12.09 ± 0.40	0.06 ± 0.00
OM (%)	73.04 ± 0.20	90.91 ± 0.88	65.12 ± 1.00	ND
TP (g/kg)	29.38 ± 1.70	4.18 ± 0.37	5.47 ± 0.45	0.52 ± 0.06
TKN (g/kg)	26.11 ± 0.09	1.03 ± 0.07	6.26 ± 1.24	0.93 ± 0.06
TK (g/kg)	12.54 ± 0.39	0.80 ± 0.00	74.79 ± 4.74	0.69 ± 0.03

ND (Not detected), EC (Electrical conductivity), OM (Organic matter), TP (Total phosphorus), TKN (Total Kjeldahl nitrogen) and TK (Total potassium). Results are the mean of three replicates and error bars indicate standard deviation.

2.3. Analytical methods and analysis

The collected fresh samples mentioned above were used to detect the pH, electrical conductivity (EC), dissolve organic carbon (DOC) and seed germination index (GI) as per the laboratory procedures (Li et al., 2012; Wang et al., 2016b). An MP521 pH/EC meter (Shanghai, China) was used to measure the pH and EC according to Li et al. (2015). To determine the DOC, the extraction procedure was depended on our previous method (Wang et al., 2016a), and then detected by using the automated TOC analyzer (Shimadzu TOC-V). The humic acid (HA), fulvic acid (FA), HA-complexed Cu, HA-complexed Zn, FA-complexed Cu, FA-complexed Zn and water soluble HMs (Cu and Zn) were extracted and determined according to Kang et al. (2011). The organic matter (OM), total organic carbon, total Kjeldahl nitrogen (TKN), total phosphorus, total potassium, available phosphorus and potassium were analyzed according to test methods for the composts examination (TMECC, 2002). Ammonia gas was trapped in boric acid solution and then measured by titrated with 1 mol/L hydrochloric acid (Yang et al., 2015). The N_2O samples were collected daily in the first two weeks and two or three times weekly thereafter, while the gases concentrations was determined using gas chromatography (Agilent Technologies 6890N Network GC system, China) as reported by Awasthi et al. (2016c). The biochar C, H and O properties were analyzed using Vario EL cube CHNOS element analyzer (Elementar, Germany), while BET surface area was determined according to Mc-Naughton (1976).

2.4. Statistical analysis

All of the physic-chemical analyses were repeated three times. The data were superintend to the one-way analysis of variance (ANOVA) and multiple comparison test to compare the least significance difference at $p = 0.05$ using SPSS v.18.0 software for windows. The redundancy analyses (RDA) was performed to find out the correlation of physiochemical properties, N_2O and NH_3 emission during the composting using Canoco 5 software.

3. Results and discussions

3.1. Effect of additives on cumulative NH_3 and N_2O emissions

NH_3 emission is an inevitable problem during the composting process which would not only cause the environmental pollution, but also decrease the final quality of compost (Chan et al., 2016; Wang et al., 2016b). The evolutions of cumulative NH_3 emission in all treatments are presented in Fig. 1a. At the beginning of composting, the rapid NH_3 emission in all treatments was likely due to the fast organic matter degradation and high temperature (Yang et al., 2015; Jiang et al., 2016a). The cumulative NH_3 emission from all treatments quickly increased to 8.09, 6.76, 7.21 and 3.58 g in control, B, Z and B + Z applied treatments, respectively, on day 8. The similar observation was also reported by Chowdhury et al. (2014) who adding biochar and adjusting the aeration flow rate to reduce the GHGs and ammonia emissions during cattle manure composting. After eight days, the cumulative NH_3 emission in B, Z and B + Z applied treatments tended to be stable or slightly increased, while the cumulative NH_3 emission in control treatment continuously rose and then leveled off until the end of composting. The longer duration of high temperature (> 50 °C) in control (data not show) might explained this phenomena. At the end of the experiment, the cumulative NH_3 emission was in the order of control (10.93 g) > Z (7.53 g) > B (7.01 g) > B + Z (4.00 g). And compared to the control, the cumulative NH_3 emission in B, Z and B + Z applied was reduced by 35.88%, 31.13% and 63.40%, respectively. Similar reduction was also observed by Fukumoto et al. (2011) and Awasthi et al. (2016a) for swine manure and SS composting. Biochar and zeolite have the high porosity and large specific surface which could effectively adsorb the NH_3 and NH_4^+-N and consequently

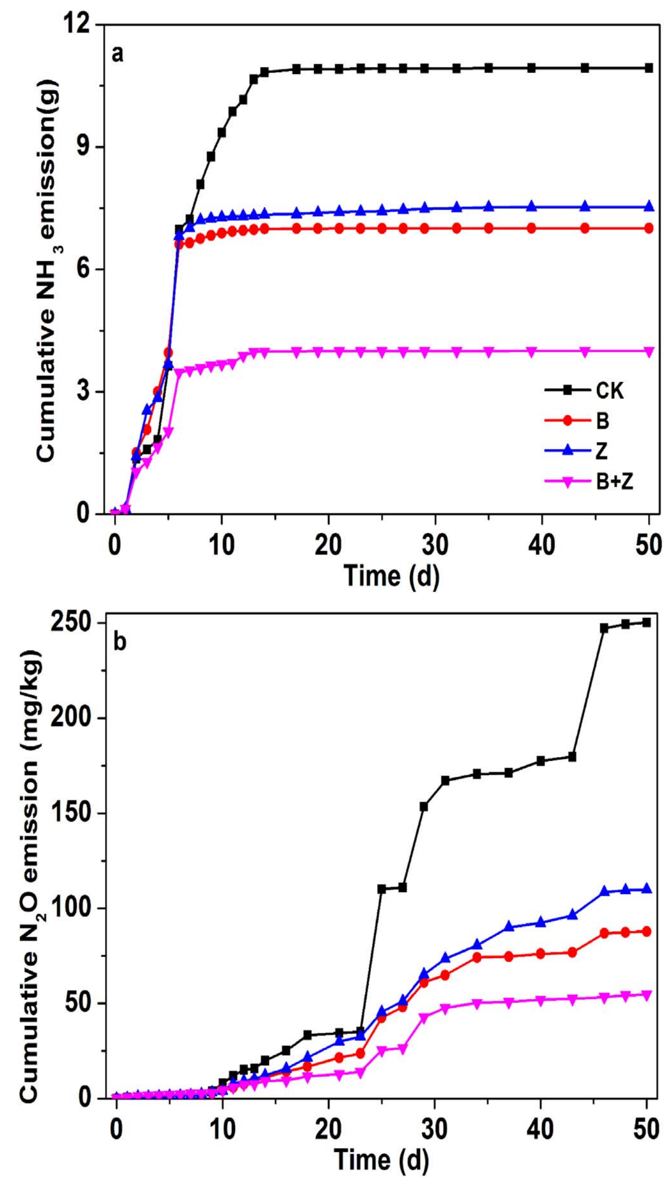

Fig. 1. Changes of cumulative NH_3 (a) and N_2O (b) emission during pig manure composting. Control: pig manure + wheat straw; B: pig manure + wheat straw + 10% biochar; Z: pig manure + wheat straw + 10% zeolite; B + Z: pig manure + wheat straw + 10% biochar + 10% zeolite.

decreased the NH_3 emission during the organic solid waste composting (Li et al., 2015; Chan et al., 2016). In addition, the effects of negative ions on the surface of biochar and the molecular sieve of zeolite could also contribute to the adsorption of ammonia (Awasthi et al., 2016c). While, compared to the B and Z applied treatment, the cumulative NH_3 emission in B + Z amended treatment was lower ($p < 0.05$), which was in consist with Awasthi et al. (2016c) and Zhang and Sun (2017a), who discovered that the combined addition of additives could further improve the nutrient transformation and reduce the nitrogen loss as compared to adding the single additive.

The variations of cumulative N_2O emission in all treatments are presented in Fig. 2b. At the initial phase of composting, the cumulative N_2O emission of all treatments was very low, which could reflect the minimal N_2O emission in this period. The similar result was also reported by Fukumoto et al. (2011) and Lopez-Cano et al. (2016) for swine manure and olive mill wastes composting. At the start of the experiment, the high temperature, ammonium and pH (data not show) would inhibit the activity of nitrifying microorganism and then resulted

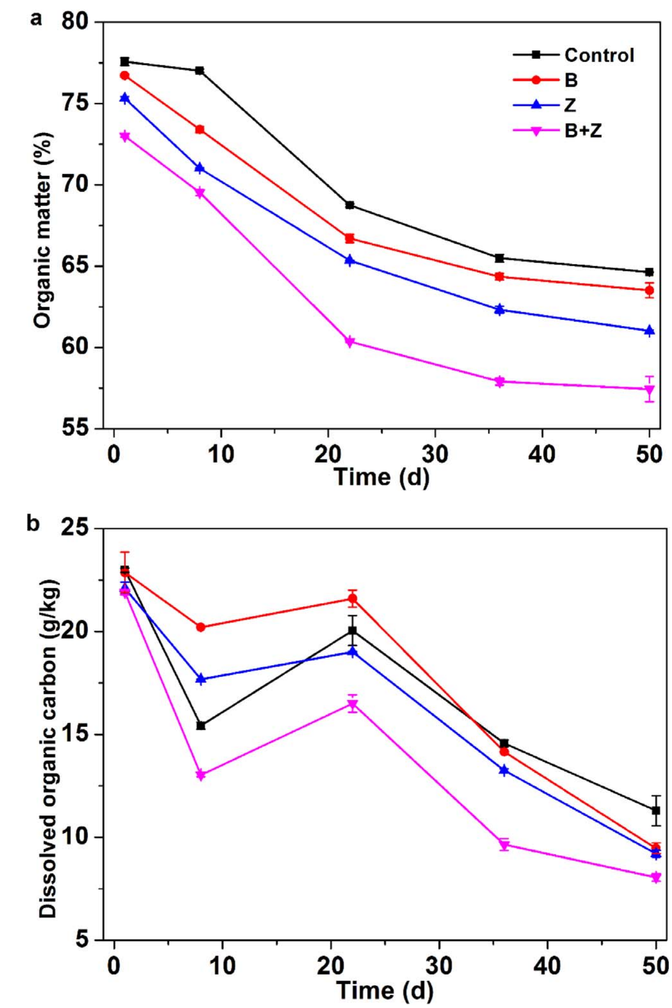

Fig. 2. Evaluation of organic matter (a) and dissolved organic carbon (b) during the pig manure composting. Control: pig manure + wheat straw; B: pig manure + wheat straw + 10% biochar; Z: pig manure + wheat straw + 10% zeolite; B + Z: pig manure + wheat straw + 10% biochar + 10% zeolite. Results are the mean of three replicates and error bars indicate standard deviation.

in the minor N_2O emission (Sommer and Moller, 2000; Wang et al., 2013). On the other hand, the low content of nitrate at the beginning of composting could render the heterotrophic denitrifiers inactive (Awasthi et al., 2016c; Jiang et al., 2016b). After 8 days, the cumulative N_2O emission gradually increased and occurred a significant N_2O emission on day 22–36. The similar increase of cumulative N_2O emission in all treatments was also observed by Luo et al. (2013), who used the phosphogypsum and dicyandiamide to reduce the N_2O emission during the PM composting. And the high N_2O emission in this period (cooling and mature phases), might be due to temperature decrease and the nitrification of ammonium (Yang et al., 2015; Wang et al., 2016b). In addition, nitrate produced in this phase might by diffusion or mass flow move to anaerobic zones and then denitrified to N_2O and N_2 (Sommer and Moller, 2000).

Throughout the composting process, the cumulative N_2O in control was higher ($p < 0.05$) than other additives amended treatments, which was correspond with Chowdhury et al. (2014) and Awasthi et al. (2016c), who added the biochar and zeolite to reduce the GHGs emission during cattle manure and SS composting. Wang et al. (2013) also indicated that the addition of alkaline materials such as biochar could inhibit the N_2O emission during the PM composting. At the end of the experiments, the cumulative N_2O emission was 250.29, 87.83, 110.0 and 54.73 mg/kg in control, B, Z and B + Z applied treatments, respectively. And compared to the control, the cumulative N_2O emission was decreased by 64.91, 56.05 and 78.13% in B, Z and B + Z amended treatments, respectively. Similar reduction was also observed by Jiang et al. (2016a) for co-composting of PM with dicyandiamide and Awasthi et al. (2016c) for SS and mixture additives (biochar + zeolite) composting.

3.2. Effect of additives on organic matter and dissolved organic carbon transformation

The variations of organic matter (OM) content are presented in Fig. 2a. During the composting process, OM content of all treatments gradually decreased with composting processed, possibly due to the microorganism utilized the OM as their energy sources and emitted the CO_2 (Bernal et al., 2009; Awasthi et al., 2016a; Wang et al., 2016b). Compared to the control and B added treatments, the initial OM content of Z and B + Z was distinctly ($p < 0.05$) lower, might be due to the zeolite has the negligible content of OM. The similar results were also reported by Li et al. (2012) and Wang et al. (2016a) for PM composting amended with bentonite. From the beginning of composting, the OM content in B, Z and B + Z amended treatments decreased faster than control, which were also resulted in the higher temperature and pH values (data not show). After 22 days, OM contents of all treatments obviously declined and then trended to stable at the end of composting.

Finally, OM content in B, Z and B + Z was 63.51%, 61.02% and 57.43%, respectively, which were lower ($p < 0.05$) than the control treatment (64.62%). As Dias et al., 2010 and Zhang and Sun (2015) indicated that biochar and zeolite amendment could accelerate the OM degradation during the poultry and green waste composting. Among the all treatments, the highest OM reduction was observed in B + Z applied treatment (15.57%), and followed by Z (14.30%), B (13.22%) and control (12.95%). The results revealed that biochar combined with zeolite could remarkably ($p < 0.05$) facilitate the OM mineralization as compared to the B and Z added treatments, which might be due to the mixture additive addition could further increase the porosity of substrate and stimulate the microbial activities (Awasthi et al., 2016c; Zhang and Sun, 2017b).

The changes of DOC concentration in all treatments were presented similar trend during the PM composting (Fig. 2b). At the initial phase, DOC concentration of all treatments sharply decreased and then elevated during the successive time for about 2–3 weeks. A similar profile was also reported by other researches (Gomez-Brandon et al., 2008; Wang et al., 2016b), for cattle manure and PM composting. The DOC declined during the first few days was conceivable due to the rapid decomposition of available organic carbon and as consequence caused the temperature increased as well as higher CO_2 emission (data not show). And among the all treatments, the B + Z added treatments showed the maximum DOC mineralization during the first week, which could be attributed due to the rapid microbial activities (Khan et al., 2014). Along with the composting processed, the solid polymeric material in composting matrixes continuously decreased and then released soluble organic matter which could be accounted for the DOC increase at the later phase of composting (Gomez-Brandon et al., 2008; Wang et al., 2016a). After 22 days, DOC concentration of all treatments gradually declined and then stabilized at the end of composting.

Throughout the entire composting process, the DOC contents in control, B, Z and B + Z applied treatments dropped from 22.98, 22.87 22.1 and 21.91 g/kg to 11.30, 9.46, 9.20 and 8.75 g/kg, respectively. Compared to the control (50.84%), the degradation rates of B (58.60%), Z (58.37%) and B + Z (60.04%) were significantly ($p < 0.05$) higher. This result showed that the addition of biochar and zeolite could notably improve the organic matter decomposition, which was in according with the results of Dias et al., 2010 and Awasthi et al. (2016c), who used the biochar and biochar combined with zeolite as additives for poultry manure and sewage sludge composting. Meanwhile, Bernal et al. (2009) and Wang et al. (2016b) stated that the DOC concentration of mature compost should be less than 10.0 g/kg. At the end of the experiment, only the B, Z and B + Z added treatments reached this requirement (< 10 g/kg), which could indicated that the addition of biochar, zeolite and their mixture could reduced the maturity period of composting.

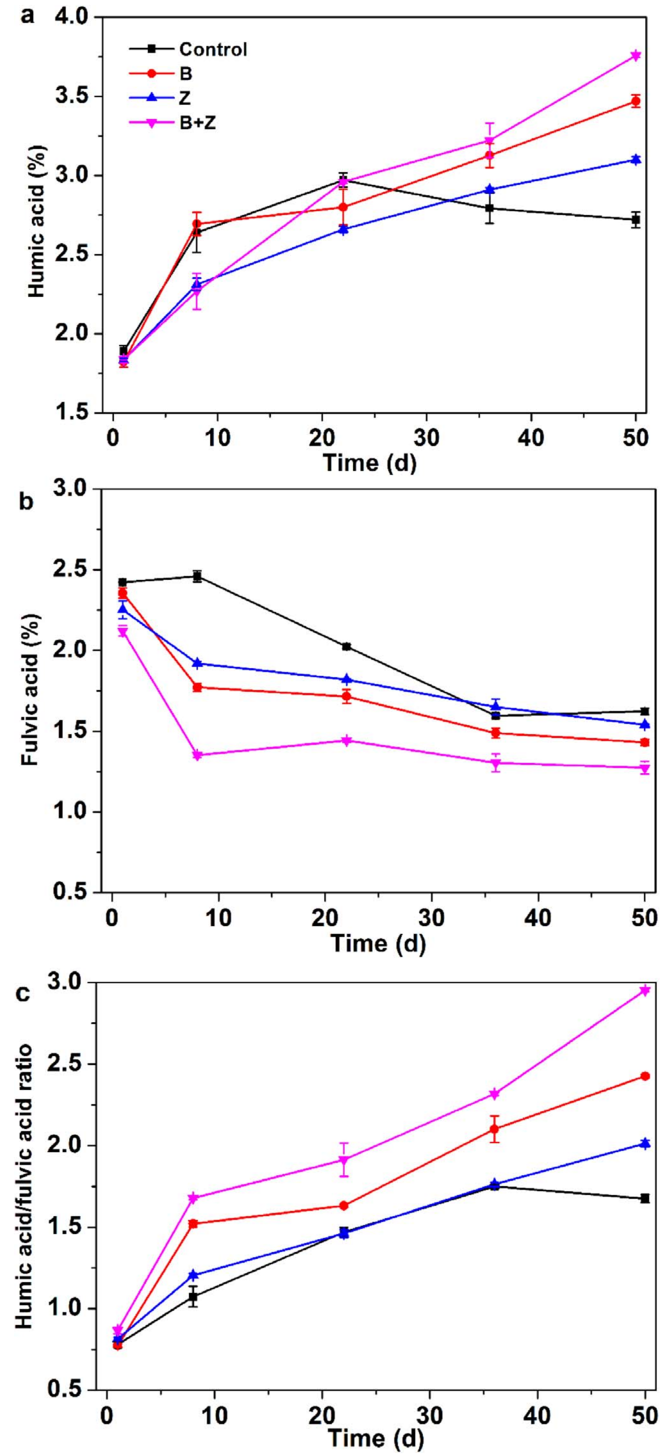

Fig. 3. Changes of humic acid (a), fulvic acid (b) and humic acid to fulvic acid ratio (c) during pig manure composting. Control: pig manure + wheat straw; B: pig manure + wheat straw + 10% biochar; Z: pig manure + wheat straw + 10% zeolite; B + Z: pig manure + wheat straw + 10% biochar + 10% zeolite. Results are the mean of three replicates and error bars indicate standard deviation.

3.3. Effect of additives on humification during the composting

Humic acid (HA) and fulvic acid (FA) are the main components of the humic substrates, which could indicate the maturity and stabilization of compost (Dias et al., 2010). In general, the mature compost always contain the high content of HA and the low content of FA (Zhang and Sun, 2015). The results of this study were in line with that generalization in that the HA in all treatment gradually increased while the FA continuously declined (Fig. 3a and b). At the beginning of composting, the HA content among the all treatments rapidly increased, while the HA content in additives (B, Z and B + Z) amended treatments was lower than the control, probably due to the addition of biochar and zeolite could obviously improve the readily available organic matter degradation at the initial phase of composting (Zorpas and Loizidou, 2008; Awasthi et al., 2016a) and consequently result in the lower rate of HA formation than degradation.

The similar result was also observed by Wang et al. (2014) for co-composting of PM and biochar, and Zhou et al. (2014) for food waste and Chinese medicinal herbal residues composting. After 22 days, the HA in control treatment slightly decreased, while went on increasing in B, Z and B + Z applied treatments. And at the end of the experiment, the HA content increased from 1.89 to 2.72%, 1.82 to 3.47%, 1.83 to 3.1% and 1.84 to 3.76% in control, B, Z and B + Z treatments, respectively. The quantities of HA content detected in this research was similar to the content observed by Ko et al. (2008) and Xiong et al. (2010), for animal manure and SS composting. Compared to the control treatment (43.95%), the increase rate of HA in B, Z and B + Z applied treatments was significantly ($p < 0.05$) higher, and the highest increase was observed in B + Z applied treatment (104.51%). As Zhang and Sun (2015) and Jindo et al. (2016) reported that the addition of zeolite or biochar could obviously improve the HA synthesis during the green waste and poultry manure composting. While, result in this study indicated that the combined addition of biochar and zeolite could further enhance of the HA formation as compared to B and Z applied treatment. This finding was agreement with Zhang and Sun (2015), who combined use of zeolite and earthworm casts to improve the green waste composting.

The evolutions of FA in all treatments are presented in Fig. 3b. As composting progressed, the FA content in all treatments sharply declined over the first 20 days and then stabilized at the end of the experiment, which was in consist with Huang et al. (2006) and Zhou et al. (2014), for PM and food waste composting. At the initial phase of composting, the fast degradation of FA in all treatments could be due to the high temperature and microbial activity of thermophilic phase (Dias et al., 2010). Meanwhile, compared to the control treatment, the FA content in B, Z and B + Z amended treatments was lower ($p < 0.05$), which was likely due to the addition of biochar and zeolite could accelerate the easily degradable organic matter (Fig. 2b) decomposition and stimulate the activity of microbes during the composting process (Venglovsky et al., 2005; Li et al., 2015). After three weeks, with the temperature and biological activities decreased, the FA content among the all treatments presented stable or slightly decreased. And at the end of composting, the FA content was reduced to 1.62%, 1.43%, 1.54% and 1.27% in control, B, Z and B + Z applied treatments, respectively. While, the maximum degradation rate was observed in B + Z (39.98%) followed by 39.31%, 34.80% and 32.99% in B, Z and control treatments.

This result was in accordance with the observation of Zhang and Sun (2015), and Awasthi et al. (2016a) who found that the addition of biochar and zeolite can promote the FA degradation during composting. The addition of mineral additives could increase the porosity of compost mixtures and then improve the soluble organic matter mineralization (Chen et al., 2010; Li et al., 2012; Wang et al., 2016b). Furthermore, the nutrients provided by the additives could also enhance the microbial metabolism and consequently accelerate the FA degradation (Gabhane et al., 2012; Jindo et al., 2016; Wang et al., 2017). Meanwhile, compared to the B and Z applied treatments, introducing the B + Z could further promote the FA decomposition, probably due to the combined addition of biocahr and zeolite may provide better composting condition (higher temperature, porosity, oxygen diffusion and microorganism activity) than adding the single additive (Zhang and Sun, 2015; Awasthi et al., 2016c).

Humic acid to fulvic acid (HA/FA) ratio has been widely used to evaluate the degree of polymerization and maturity of the composting product (Bernal et al., 2009; Jindo et al., 2016). During the experimental process, the HA/FA ratio among the all treatments gradually increased (Fig. 3c), which was in consist with the result observed by Awasthi et al. (2016c) who combined addition of lime and zeolite to improve the humification during the SS composting. The continuous increase of HA/FA ratio in all treatments could be due to the increase of the HA while the decrease of the FA during the experiment (Dias et al., 2010; Zhou et al., 2014). At the end of the composting, the highest change in B + Z applied treatment (from 0.87 to 2.95), followed by B (from 0.77 to 2.43), Z (from 0.81 to 2.01) and control (from 0.78 to 1.68), and the differences among treatments were significant ($p < 0.05$). Compared to the control, the HA/FA ratio of B, Z and B + Z amended treatments increased faster and the value of the HA/FA ratio in these treatments was also higher ($p < 0.05$), which could indicated that addition of biochar, zeolite and their mixture could promote the polymerization and humification of compost.

During the composting process, the porous mineral additives could improve the activity of microorganism and sorb humic substances on their surface, resulting in the high production of HA and biodegradation of FA or non-humic fraction in composts (Huang et al., 2006; Jindo et al., 2016; Zhang and Sun, 2017b). Generally, the HA/FA ratio of compost more than 1.6 could regard as mature (Jindo et al., 2016). Thus, in current research, the final compost in all treatments was mature, and the B + Z applied treatment presented the best maturity and humification. This result was in line with the findings of Zhang and Sun (2015), who reported that the combined addition of additives could further improve the nutrient transformation and organic humification as compared to single additive amended.

3.4. Effect of additives on complexation ability of HA and FA with metal ions

During the composting process, the HA-Cu and HA-Zn in all treatment gradually increased and then stabilized at the end of the experiment (Fig. 4a and b). The similar trend was also observed by Xiong et al. (2010) and Kang et al. (2011) for SS composting. As composting processed, the high molecular weight compounds such as phenolic and benzene-carboxylic groups increased, and produced a greater degree of polycondensed and aromatic HA (Huang et al., 2006; Wang et al., 2014). Therefore, the binding capacities and affinities of HA with the Cu and Zn promoted with composting time and consequently increased the HMs (Cu and Zn) content in the HA (Veeken et al., 2000; Kang et al., 2011). At the end of the experiment, the HA-Cu content increased from 12.24 to 54.43 mg/kg, 11.80 to 47.19 mg/kg, 11.90 to 51.10 mg/kg and 11.59 to 36.72 mg/kg in control, B, Z and B + Z applied treatments. While, the HA-Zn content of these treatments rose to 3.38, 2.46, 2.80 and 2.08 mg/kg, respectively.

Results in this study indicated that the Cu presented the better complexation abilities with HA than Zn, which was in agreement with the Plaza et al. (2006) who investigated the affinities of metal ions (Cu, Zn, Cd and Pb) with HA derived from SS and soil. Besides, Kang et al. (2011) also discovered that the Cu combined with HA more strongly than Zn during the SS composting. Meanwhile, compared to the control treatment, the final contents of HA-Cu and HA-Zn in B, Z and B + Z applied treatments were obviously ($p < 0.05$) lower, and followed the order control > Z > B > B + Z. Reasons for this phenomen might be due to the higher pH and the adsorption capacity of biochar and zeolite decreased the mobility of HMs and then resulted in the lower Cu

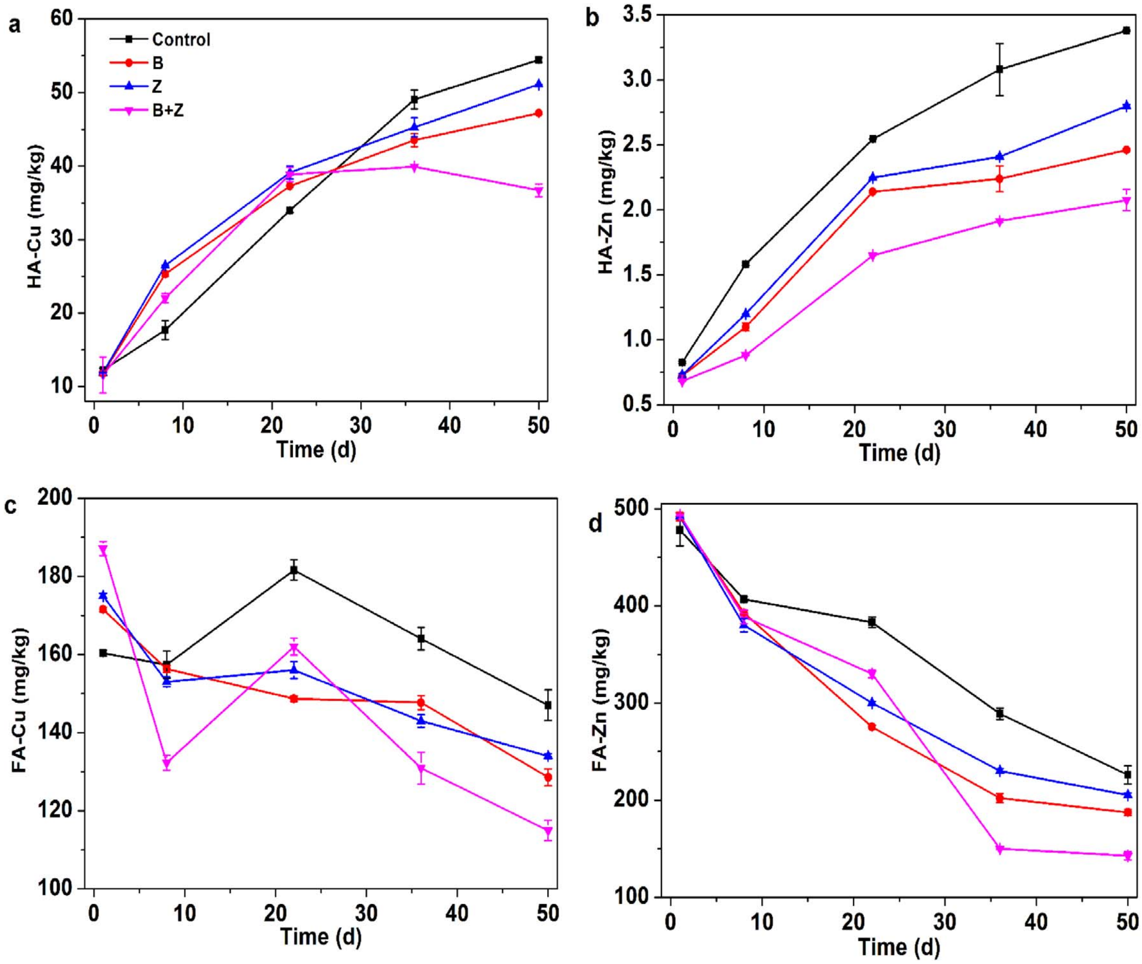

Fig. 4. Changes of HA-Cu (a), HA-Zn (b), FA-Cu (c) and FA-Zn (d) during pig manure composting. Control: pig manure + wheat straw; B: pig manure + wheat straw + 10% biochar; Z: pig manure + wheat straw + 10% zeolite; B + Z: pig manure + wheat straw + 10% biochar + 10% zeolite. Results are the mean of three replicates and error bars indicate standard deviation.

and Zn blending with HA (Zorpas and Loizidou, 2008; Li et al., 2015).

The variations of FA-Cu and FA-Zn in all treatments are shown in Fig. 4c and d. During the composting process, the FA-Zn content in all treatments continuously decreased, while the FA-Cu presented a little difference. The FA-Cu content in B and Z applied treatments gradually declined during the whole composting process, but in control and B + Z applied treatments presented an increase on day 8–22 and then declined until the end of the experiment. As composting processed, the FA-Cu and FA-Zn decreased in all treatments probably due to the FA decomposition and the FA-Cu and FA-Zn or the heavy metal ions (Cu^{2+} and Zn^{2+}) transformed to the solid phase (HA-Cu and HA-Zn) (Xiong et al., 2010; Kang et al., 2011). The observation in Fig. 4a and b also supported this evidence. While, the increase of FA-Cu content was possibly attributed to the initially fast degraded organic matter of PM and then released the Cu (Kang et al., 2011). At the end of the experiment, the FA-Cu reduced to 147.00, 128.55, 134.00, and 114.93 mg/kg in control, B, Z and B + Z applied treatments, while the FA-Zn decreased from 478.14–493.56 mg/kg to 225.99–187.42 mg/kg.

Compared to the control treatment (Cu 8.33% and Zn 52.73%), the degradation rates of FA-Cu and FA-Zn contents in B, Z and B + Z amended treatments were higher (Cu 23.43–38.58% and Zn 58.30–71.07%) and the lowest HMs content in FA was observed in B + Z applied treatment. Because of the characters of FA, such as dissolving at all pH values, containing low molecular weight acids and small degrees of aromatic ring polycondensation and polymerization, the mobility and bioavailability of HMs could be increased when associated with FA (Huang et al., 2006; Plaza et al., 2006; Kang et al., 2011). Therefore, the result indicated that the mobility of HMs could be decreased after composting and the addition of biochar, zeolite and their mixture could further improved the immobilization of HMs (Cu and Zn). This finding was in line with the previous researches (Zorpas and Loizidou, 2008; Li et al., 2015; Awasthi et al., 2016b).

3.5. Correlation of analyzed parameters

As showed (Fig. 5), the RDA was conducted to find out the relationship of gaseous emission, humification and organic matter degradation in each treatment. The RDA confirmed that, significantly ($p < 0.05$) maximum 87.22% relation was observed in only 10% B followed by 83.65% B + Z and 79.08% 10% Z alone blended treatments, respectively, while drastically very low correlation was observed in control treatment by 67.78% might be due to slow degradation and humification (Fig. 5). The RDA percentage of correlation between the NH_3 emission, humification and organic matter transformation were in all treatments not only showed the rate of mineralization, but also indicated that closely related with overall gaseous emission and stabilization of end product. Similarly, Awasthi et al. (2016a) and Wang et al. (2017) also revealed that gaseous emission, temperature and physicochemical transformation such as OM, DOC and C/N ratio were provide the overall information about rate of composting and promote compost applicability for organic farming. Furthermore, Awasthi et al. (2016c) has been observed that dosage of additives (12% biochar mixed with different concentration of zeolite) and how often influenced the gaseous emission, temperature, pH, enzymatic activities, water soluble, total

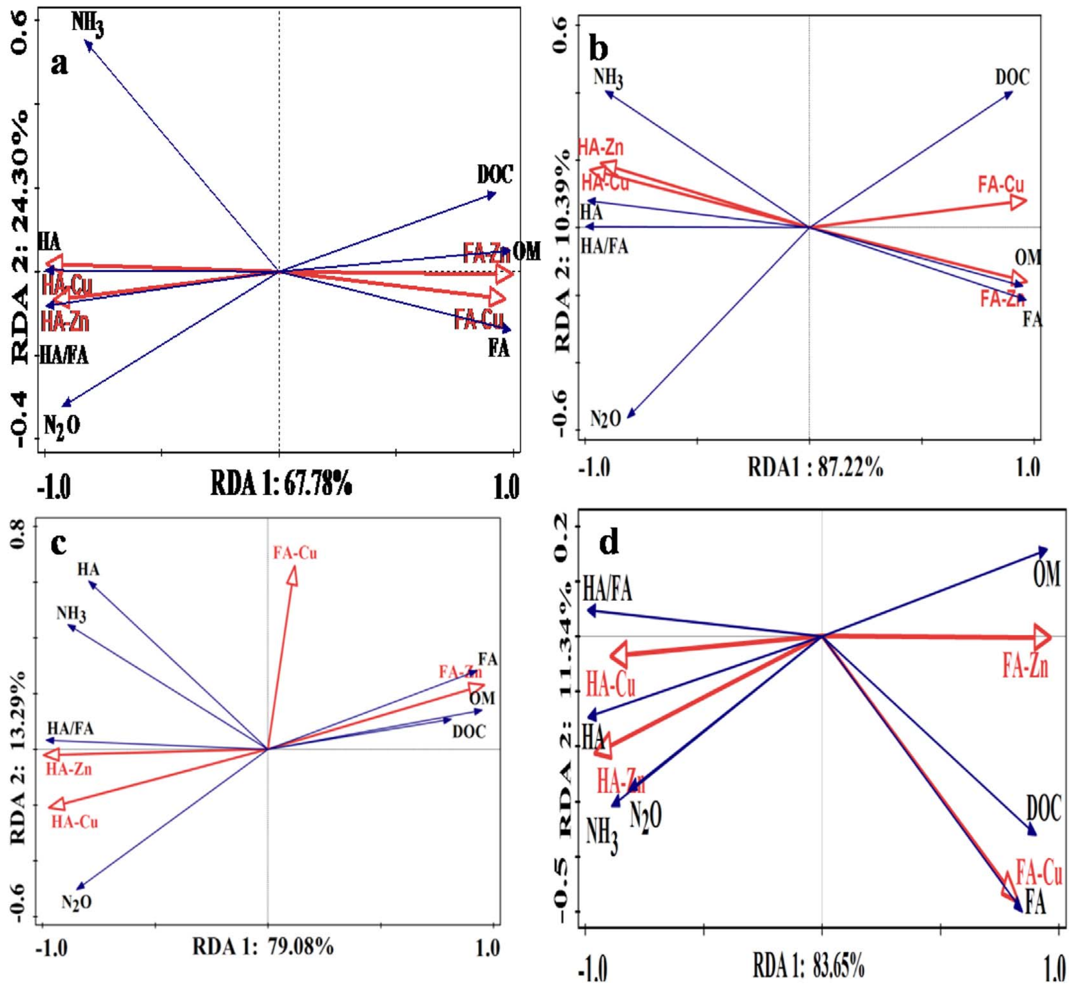

Fig. 5. Redundancy analysis (RDA) of physiochemical properties, N_2O and NH_3 emission during the composting. Control (a), 10% biochar (b), 10% zeolite (c) and 10% biochar + 10% zeolite (d).

nutrients profile and GI during the SS composting.

3.6. Nitrogen balance

As shown in Table 2, the nitrogen loss in all treatments ranged from the 19.72 to 26.78%, which was lower than the results observed in pervious researches (Chowdhury et al., 2014; Jiang et al., 2015; Jiang et al., 2016a). While, the total nitrogen losses in this study was felt right into the range (16–79%) founded by Barrington et al. (2002), for swine manure composting. The different losses of these studies could be due to the difference in composting materials, aeration conditions and manual handling (Jiang et al., 2016a; Awasthi et al., 2017a,b). Compared to the control treatment, the addition of B, Z and B + Z could significantly ($p < 0.05$) decrease the nitrogen loss, and the lowest nitrogen loss (19.72%) was recorded in B + Z applied treatment. The resembled result was also report by Yang et al. (2015), for PM and phosphogypsum composting, and Awasthi et al. (2017a,b) for co-composting SS with high dosage (8–18%) of biochar. In addition, Jiang et al. (2016a) reported that the combined addition of additives could further decrease the nitrogen loss during the PM composting. While, in this research, the total NH_3 and N_2O emissions of all treatments accounted for 0.86–2.48% and 0.19–0.79% of the initial nitrogen, which was in line with Jiang et al. (2014) and Awasthi et al. (2017a,b) for PM and SS composting.

Table 2
Nitrogen balance.

Treatment	N balance				
	TN losses (% initial TN)	NH_3 losses (% initial TN)	N_2O losses (% initial TN)	NH_4^+ in water trap	N unaccounted for (% initial TN)
Control	26.78 ± 0.10	2.48 ± 0.01	0.79 ± 0.01	0.03 ± 0.01	23.50 ± 0.11
B	22.46 ± 0.05	1.57 ± 0.00	0.30 ± 0.03	0.01 ± 0.00	20.59 ± 0.05
Z	23.10 ± 0.01	1.74 ± 0.01	0.39 ± 0.02	0.01 ± 0.00	20.97 ± 0.03
B + Z	19.72 ± 0.02	0.86 ± 0.02	0.19 ± 0.00	0.02 ± 0.00	18.66 ± 0.01

TN losses (%) = 100 (initial TN − final TN)/initial TN, N unaccounted for = TN losses − NH_3 losses − N_2O losses. Control: pig manure + wheat straw; B: pig manure + wheat straw + 10% biochar; Z: pig manure + wheat straw + 10% zeolite; B + Z: pig manure + wheat straw + 10% biocahr + 10% zeolite. Results are the mean of three replicates and error bars indicate standard deviation.

Table 3
Selected compost maturity and nutrient parameters of the final composts.

Parameter	Control	B	Z	B + Z	TMEC (2002)
pH	7.96 ± 0.04	8.50 ± 0.03	8.52 ± 0.01	8.60 ± 0.02	5.5–8.5
C:N ratio (dw)	17.00 ± 0.21	16.77 ± 0.54	16.85 ± 0.21	17.62 ± 1.01	≤25
OM (%)	64.62 ± 0.01	63.51 ± 0.46	61.02 ± 0.06	57.44 ± 0.78	≥40
Germination index (%)	93.06 ± 5.61	99.34 ± 1.72	98.21 ± 2.15	102.41 ± 2.20	80–90
Water soluble Cu (mg/kg)	52.72 ± 2.34	38.66 ± 1.21	42.05 ± 1.01	29.10 ± 0.58	–
Water soluble Zn (mg/kg)	38.49 ± 1.15	25.79 ± 1.00	28.16 ± 0.21	19.58 ± 0.68	–
Available phosphorus (g/kg)	1.35 ± 0.04	1.55 ± 0.05	1.53 ± 0.02	1.56 ± 0.05	–
Available potassium (g/kg)	10.38 ± 0.21	14.95 ± 0.22	14.21 ± 0.12	15.56 ± 0.23	–

Results are the mean of three replicates and error bars indicate standard deviation. Control: pig manure + wheat straw; B: pig manure + wheat straw + 10% biochar; Z: pig manure + wheat straw + 10% zeolite; B + Z: pig manure + wheat straw + 10% biocahr + 10% zeolite.

3.7. Effect of additives on the maturity and quality of final product

Pig manure compost has been widely used as soil organic fertilizer or amendment, while the low quality of compost utilization would be harmful to the soil and plant as well as resulting in the environmental risk, hence before its application, the maturity and quality of compost is essential to be assessed (Li et al., 2012; Jiang et al., 2015; Wang et al., 2016a). As shown in Table 3, after composting, the final product of all treatments showed well maturity, but for B, Z and B + Z amended treatments, the pH values were slightly higher than the standard limit; however, the final GI values of B, Z and B + Z applied treatments were higher ($p < 0.05$) than the control and standard limit, which stated that the final products were non-phytotoxic and matured. The result was in line with Li et al. (2015), who also identified that pH or EC is not only criteria for compost maturity, if GI value higher than standard limit for PM composting amended with biochar. Consequently, the total available nutrients (phosphorus and potassium) of B, Z and B + Z applied treatments were significantly higher ($p < 0.05$) than control, which was likely due to biochar and zeolite could improve the OM degradation and microbial activities (Jindo et al., 2012; Chan et al., 2016).

Meanwhile, the biochar and zeolite also could release the nutrients and then raise the available nutrients (Zhang and Sun, 2015; Khan et al., 2016). In addition, compared the B and Z amended treatments, the seed germination index and available nutrients in B + Z added treatment was higher, which was in consist with Zhang and Sun (2017b), who indicated that combined addition of seaweed and bentonite could further improve the composting process and increase the final quality of end product as compared to adding the single additive. On the other hand, compared to the control treatment, the addition of B, Z and B + Z could significantly decrease ($p < 0.05$) the water soluble HMs (Cu and Zn) contents, and the B + Z added treatment presented the lowest water soluble HMs contents. This observation was in consist with Zorpas and Loizidou (2008) and Li et al. (2015), who discovered that the addition of biochar and zeolite could decrease the mobility of HMs during the PM and SS composting. Consequently, the addition of biochar, zeolite and their mixture had no negative effect on the maturity of compost, but improved the nutrients contents and compost quality.

4. Conclusion

The addition of B, Z and B + Z has positive effect to improve the organic matter degradation and humification as well as increase the available nutrient contents as compared to control. Among the all treatments, the highest HA content and HA/FA ratio was observed in B + Z applied treatment. Meanwhile, adding the B + Z further decreased the nitrogen loss and the binding ability of HA and FA with HMs (Cu and Zn). Moreover, the B + Z added treatment showed the lowest NH_3 and N_2O emissions during PM composting. Therefore, combined use of B + Z could be more potentially to improve the PM composting and compost quality.

Acknowledgements

This research was funded by the Chinese Universities Scientific Fund (No. 2452016068) and China Postdoctoral Science Foundation (No. 2016M602865).

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