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Heterogeneity of zeolite combined with biochar properties as a function of sewage sludge composting and production of nutrient-rich compost

Mukesh Kumar Awasthi [a,b], Meijing Wang [a], Ashok Pandey [c], Hongyu Chen [a], Sanjeev Kumar Awasthi [d], Quan Wang [a], Xiuna Ren [a], Altaf Hussain Lahori [a], Dong-sheng Li [a], Ronghua Li [a], Zengqiang Zhang [a,*]

[a] *College of Natural Resources and Environment, Northwest A&F University, Yangling, Shaanxi Province 712100, PR China*
[b] *Department of Biotechnology, Amicable Knowledge Solution University, Satna, India*
[c] *Centre for Innovative and Applied Bio-processing (CIAB), Mohali, Punjab, India*
[d] *International Institute of Waste Management (IIWM), Bhopal, India*

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ABSTRACT

In the present study, biochar combined with a higher dosage of zeolite (Z) and biochar (B) alone were applied as additives for dewatered fresh sewage sludge (DFSS) composting using 130-L working volume lab-scale reactors. We first observed that the addition of a mixture of B and Z to DFSS equivalent to 12%B + 10% (Z-1), 15% (Z-2) and 30% (Z-3) zeolite (dry weight basis) worked synergistically as an amendment and increased the composting efficiency compared with a treatment of 12%B alone amended and a control without any amendment. In a composting reactor, the addition of B + Z may serve as a novel approach for improving DFSS composting and the quality of the end product in terms of the temperature, water-holding capacity, CO_2 emissions, electrical conductivity, water-soluble and total macro-nutrient content and phytotoxicity. The results indicated that during the thermophilic phase, dissolved organic carbon, NH_4^+-N and NO_3^--N increased drastically in all biochar amended treatments, whereas considerably low water-soluble nutrients were observed in the control treatment throughout and at the end of the composting. Furthermore, the maturity parameters and dissolved organic carbon (DOC) indicated that compost with 12%B + 15%Z became more mature and humified within 35 days of DFSS composting, with the maturity parameters, such as CO_2 evolution and the concentration of NH_4^+-N in the compost, being within the permissible limits of organic farming in contrast to the control. Furthermore, at the end of composting, the addition of higher dosage of biochar (12%) alone and 12% B + Z lowered the pH by 7.15 to 7.86 and the electrical conductivity by 2.65 to 2.95 mS cm^{-1} as compared to the control, while increased the concentrations of water-soluble nutrients (g kg^{-1}) including available phosphorus, sodium and potassium. In addition, greenhouse experiments demonstrated that the treatment of 150 kg ha^{-1} biochar combined with zeolite and that of 12%B alone improved the yield of Chinese cabbage (*Brassica rapa chinensis* L.). The highest dry weight biomass (1.41 ± 0.12 g/pot) was obtained with 12%B + 15%Z amended compost. Therefore, 12%B + 15%Z can be potentially applied as an amendment to improve DFSS composting.

1. Introduction

One of the most problematic characteristics of human society is its capacity to utilize huge quantities of water for anthropogenic activities and later generate large amounts of waste water, which cause serious environmental problems, such as sewage sludge (SS). In China, more than 129 million tons of municipal wastewater are treated daily in wastewater treatment plants (WWTPs). During this process, over 30 million tons of SS are generated annually as an unavoidable byproduct (National Bureau of Statistics of the People's Republic of China, 2014). The management of huge quantities of biological SS from waste-water treatment plants is an expansive and environmentally sensitive problem in Chinese cities because this waste contains heavy metals (HMs), organic micro-pollutants and pathogens, which have lead to stringent legislation for SS applications (Zhang et al., 2014; Awasthi et al., 2016b).

However, in the last few years, many alternative methods for the ecofriendly disposal of this bio-waste have been proposed, with composting being one of the most promising alternative technologies used to kills pathogens present in these waste materials. Composting has the ability to create a valuable humus-like end product that can be used as a growing medium (Malinska et al.,

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

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2014; Zhang et al., 2016) or increase soil fertility (Biederman and Harpole, 2013). In fact, it has been documented that the composting of SS (which is significantly rich total nitrogen and high moisture content) together with organic bulking waste materials which high contain carbon and low in moisture content (straw, rice husk, yard waste, sawdust, etc.) can be used to produce sanitized and stabilized end products by adjusting the moisture content (~55%) and carbon-to nitrogen (C/N) ratio (~25). SS mixed with wheat straw, rather than either waste alone, is more suitable for efficient composting (Venglovsky et al., 2005; Zorpas and Loizidou, 2008; Villaseñor et al., 2011; Zhao et al., 2013; Awasthi et al., 2016b).

Biochar is composed of a carbonaceous solid byproduct which formed during bio-energy production through organic biomass pyrolysis or gasification under low oxygen conditions (IBI, 2012). It has appreciable carbon sequestration value and abundant quantities of recalcitrant aromatic ring structures (Zhang et al., 2014) that have a long half-life in soil (Czekala et al., 2016). In the last few years, biochar has been widely used in soil remediation, carbon sequestration, and the mitigation of greenhouse gases (GHGs) (Shrestha et al., 2010; Jindo et al., 2012; Malinska et al., 2014; Sun et al., 2016b), because biochar sequestration and application do not require advanced scientific method. Biochar production is a simple technology and suitable for all developed as well as developing countries, but its optimization and economic feasibility for large-scale production still need to be established (Zhang et al., 2016). The biochar amendment process was applied to the composting of various organic substances by several earlier researchers (Hua et al., 2009; Dias et al., 2010; Steiner et al., 2010; Jindo et al., 2012; Awasthi et al., 2017), who reported a number of additional benefits, such as increased nutrient availability, microbial activity, soil organic matter, and water retention during organic waste composting.

Consequently, biochar can be used as a bulking agent to reduce the bulk density and increase the porosity (Steiner et al., 2010; Sun et al., 2016a), and, as a result, increase the microbial growth and enzymatic activities (Jindo et al., 2012), and reduced the nitrogen loss, CH_4 and N_2O emission (Awasthi et al., 2017), and water-soluble salts (Hua et al., 2009). In addition, Dias et al. (2010) and Zhang et al. (2016) reported that the addition of wood biochar could enhance organic-matter degradation by 73.2% of the initial content when poultry manure was mixed with wood biochar at a proportion of 1:1 (fresh weight basis). In contrast, when sawdust and coffee husk as bulking agents were amended with poultry manure, degradation levels of organic matter of 65.0% and 84.2% were achieved, respectively. A review of the above literatures indicated that the effect of natural additives such as zeolite have been extensively studied on different aspects of the composting process, such as the reduction of ammonia emissions and HMs bioavailability (Villaseñor et al., 2011; Zhao et al., 2013; Zhang et al., 2016), kaoline, bentonite, lime, phosphogypsum and medical stones for nutrient transformation and humification (Li et al., 2012; Fang and Wong, 1999; Gabhane et al., 2012; Zhang et al., 2014; Wang et al., 2016b). In the last few years, biochar has also been widely utilized as amendment for the mitigation of GHGs emission and bioavailability of HMs (Prost et al., 2013; Sánchez-García et al., 2015; Awasthi et al., 2016a). However, Jindo et al. (2012) and Zhang et al. (2016) investigated the effects of a 2–10% (v/v) wood biochar and 5–15% (v/v) wheat straw biochar amendment in poultry manure compost and found a 10% increased in the carbon content in water-extracted humic-like substances and 30% decreased in the dissolved carbon content.

However, knowledge of the effects of biochar combined with natural zeolite on nutrient transformation and compost quality during the SS composting is limited because the efficiency of composting process can observed by the rate of nutrient loss and availability of nutrients. It was with this background that wheat straw biochar mixed with SS-wheat straw to be composted to investigate its role on the biodegradation of organic matter and mitigation of GHGs as well as optimum dosage of biochar (Awasthi et al., 2017). Zeolite is a large group of microporous, hydrated aluminosilicate minerals that has the ability to reduce the various gases emissions and salinity and increased the bioavailability of mineral nutrients during composting (Munthali et al., 2014). However, zeolite alone is not good enough to buffer against the low pH during composting as revealed by several earlier authors (Venglovsky et al., 2005; Zorpas and Loizidou, 2008; Villaseñor et al., 2011; Awasthi et al., 2016b). Hence, we hypothesized that the characteristics of biochar combined with zeolite in the composting process may provide valuable information regarding the evolution of the rate of composting; considerably buffer the composting mass, water-soluble and total nutrient transformation and finally the end product quality. It should however be noted that this study was confined to the physicochemical transformation and end product quality. The objective of present study was to study the nutrient transformation during composting of DFSS with the assistance of biochar combined with a higher dosage of zeolite and compared with biochar alone as well as control treatments. The novelty of this work consists of its use of biochar combined with higher dosage of zeolite for DFSS composting and evaluating the effect of the final compost to Chinese cabbage (*Brassica rapa chinensis* L.) growth to assess the compost toxicity.

2. Materials and methods

2.1. Composting feed stock collection, processing and properties

DFSS was collected from a local municipal wastewater treatment plant (Yangling, Shaanxi Province, China) and wheat straw (WS) was collected from the local agricultural farmer of the university campus. Chopped WS (2–5 cm) was used as a bulking agent to achieve the moisture content (~55%) and C/N ratio ~25, whereas DFSS and WS were mixed at a ratio of 1:1 (dry weight basis). Biochar was purchased from Yangling Pvt. Ltd., Shaanxi Province, China, whereas natural zeolite with a cation exchange capacity of 120–160 meq/100 g and diameter of 3.5–4.0 (Ai) was purchased from Zhejiang Shenshi Mining Industry Co., Ltd, China. The biochar was prepared from wheat straw biomass via slow and dry pyrolysis at a temperature of 500–600 °C at atmospheric pressure for 24 h, which was initiated by the pyrolysis of feedstock from the bottom of the kiln as per Khan et al. (2015). The some basic properties of the biochar are shown in Table 2, and the BET surface area ($421.57\ m^2\ g^{-1}$), the pore volume ($0.2\ cm^3\ g^{-1}$) and the pore size (5.93 nm), S (0.17 ± 0.03%), O (15.8 ± 0.12%) and H (3.05 ± 0.06%), which were determined by standard methods (Mc-Naughton, 1976). The biochar C, H, O, N and S properties were analyzed using Vario EL cube CHNOS element analyzer (Elementar, German). Air-dried wheat-straw biochar was crushed into fine particles and sieved to 2–5 mm and was used as an amendment for the experiment. The basic physicochemical characteristics of the raw materials are listed in Table 2.

2.2. Composting system and experimental design

Composting was carried out in 130-L laboratory scale in-vessel reactors which is filled with 100-L or ~50 kg of fresh DFSS mixed with wheat-straw (1:1 ratio on dry weight basis or ~5:1 ratio of fresh weight basis), and 12% B combined with different dosages of Z [10% (Z-1), 15% (Z-2) and 30% (Z-3) by dry weight of the DFSS] (Table 1). Similarly 100-L mixture of DFSS and WS (that is, without any amendment) were used as a control, whereas a 12%B alone amended treatment served for comparison purposes. In addition,

Table 1
Treatments and the dosage of different amendments used in each treatment on dry weight basis.

Treatments	Percentage of additive amendment	
	Zeolite (%)	Biochar (%)
DFSS + WS (C)	0	0
DFSS + WS + 12%B (B)	0	12
Zeolite 10% - DFSS + WS + 12%B + 10%Z (Z-1)	10	12
Zeolite 15% - DFSS + WS + 12%B + 15%Z (Z-2)	15	12
Zeolite 30% - DFSS + WS + 12%B + 30%Z (Z-3)	30	12

1 kg of plastic spheres was mixed with initial feed stock to adjust the initial bulk density to ~0.5 kg L^{-1} according to our previous work experience (Wang et al., 2013; Awasthi et al., 2015). The plastic sphere was purchase from the local market (www.taobao.com) which is non-biodegradable, octagonal shape, size 1 cm^3 and density ~0.7 g cm^{-3}. The penolics (PF) or phenol formaldehydes used for manufacture of this kind of plastic spheres which is relatively heat resistant and excellent fire resistant polymer. The 12% biochar concentration was decided on the basis of our previous study for SS composting (Awasthi et al., 2017). The systematic layout of the reactor used for the present experiment (length × width × height, 121 × 30 × 30 cm^2) is described in Fig. 1, and whirlpool pump with a gas-flow meter was used for aerating the feed stock mixtures: where as a fresh air was pumped into a reactor at the bottom of each vessel at a rate of 0.03 m^3 h^{-1} kg^{-1} (wet basis). The composting mass core temperature of each reactor was recorded daily four times (6 h) using temperature sensors, and the average temperature was reported. The composting materials were mixed thoroughly on days 0, 3, 7, 10, 14, 21, 28, 35, 42, 49 and 56 during composting. Samples were collected from each vessel and the moisture content was readjusted at 55 ± 2% (w/w, wet weight) by adding mineral free water as required. The samples collected as mentioned above were turned and uniformly mixed. One part of the fresh sample was subject to 4 °C to assess water-soluble nutrients, and another part of the samples was air dry, properly grinded by the using of mortar and pestle, and then sieved through a 0.1 mm sieve for the total nutrient content analysis. Two other parts were stored as fresh samples at −20 °C for microbiological analysis.

2.3. Analytical methods

To evaluate the carbon dioxide (CO_2) emissions, the exhausted gas was collected daily during the first 2 weeks and then 3–4 times per week using a1-LTedlar® PLV gas sampling bag w/ Thermogreen®LB-2 Septa (Sigma-Aldrich) according to the procedure of our previous study, Awasthi et al. (2016a). The data for non-measured days were calculated by averaging the closest measured days. The concentration of CO_2 was analyzed within 12 h using gas chromatography (Agilent Technologies 6890 N Network GC system, China), as explained by Colón et al. (2012). The fresh compost samples were collected after the compost materials had been turned and uniformly mixed. 1:5 aqueous extracts were obtained by shaking the samples with deionized water (1:10, w/v) at 200 rpm for 1 h in a horizontal shaker kept at room temperature. Thereafter, pH and EC was measured using a pH meter with a glass electrode (INESA PHSJ-3F, China) and conductivity electrode (INESA DDS-307, China). The filtrate of each sample was passed through a 0.45-lm polytet-rafluoroethylene filter, after which the dissolved organic carbon (DOC) and extractable ammonium (NH_4^+-N) were determined. The total organic matter (TOM), extractable ammonium (NH_4^+-N), total organic carbon (TOC), total Kjeldahl nitrogen (TKN), total potassium (TK), total sodium (TNa), total phosphorus (TP), water-soluble K^+ and Na^+, available

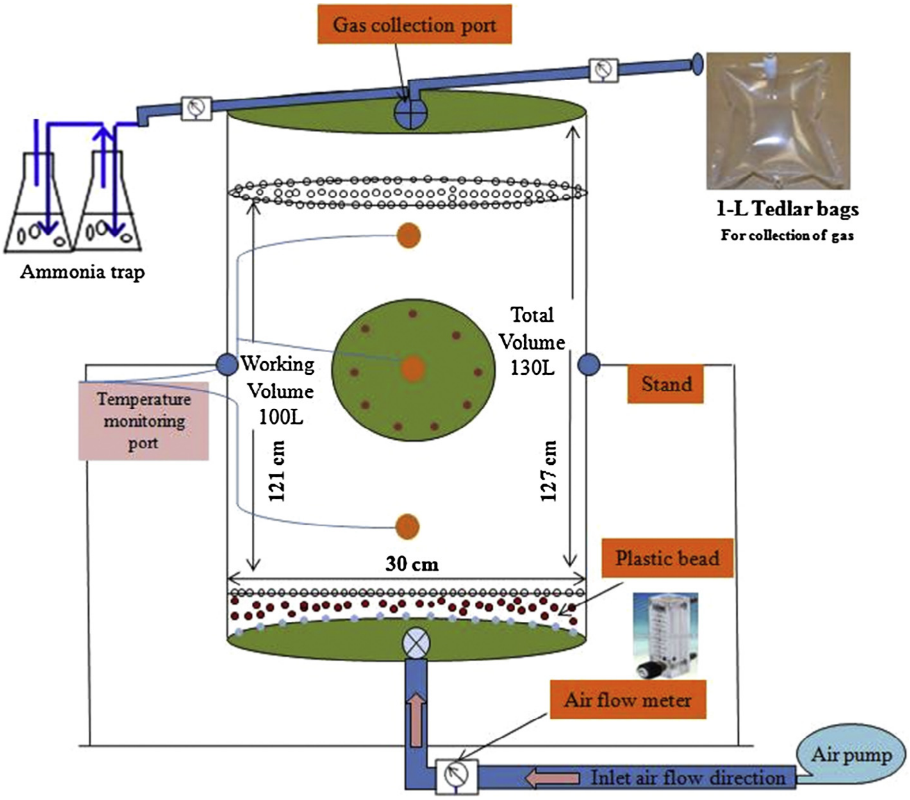

Fig. 1. Schematic diagram of the composter used in the experiment.

phosphorus (AP), and nitrate (NO_3^--N) were determined as per the standard test methods for the examination of composts and composting (TMECC, 2002). A total organic carbon analyzer (TOC-VCPH, Shimadzu, Japan) was used to measure dissolved organic carbon (DOC) and dissolved organic nitrogen (DON), whereas the NH_4^+-N concentration was analyzed by UV–vis spectrophotometer (Shimadzu UVmini-1240, Japan). The TP and AP concentration were quantified by UV–vis spectrophotometer (Shimadzu UVmini-1240, Japan). The DOC concentration and DON concentration were used to determine the soluble C/N ratio in the aqueous phase, whereas TKN and TOC were used to calculate the solid C/N ratio. The concentrations of water-extractable NO_3^--N, was measured using a cadmium reduction method, whereas the total sodium (TNa), total potassium (TK) and water-extractable K^+ and Na^+ were measured using a flame photometer (Jingke Co., Shanghai JK FP640, China). The germination test was carried out to evaluate the phytotoxic levels (Zucconi et al., 1981), using cress seeds to reveal the detoxification process. Only matured compost was used for further plant growth or greenhouse experiments. Soil properties including water holding capacity of air-dried samples was examined by OECD Guidelines 2008; and particle size of sand, silt and clay was measured using the Master size 2000E (Malvern, UK) laser diffractometer (Sochan et al., 2012), while BET surface area, pore volume and pore size were determined by Mc-Naughton (1976). Cation exchange capacity (CEC) was evaluated by USEPA Method 9080.

2.4. Greenhouse experiment

The greenhouse pot experiments were conducted using unfertile soil (0–20 cm depth), which was collected from the Northwest A&F University farmland Test Station. The physicochemical properties of the collected soil according to world reference base for soil resources are as follows: pH 7.56, EC 0.35 mS cm^{-1}, moisture 14.38%, water holding capacity (24.36%), BET surface area (2.51 $m^2\,g^{-1}$), pore volume (0.007 $cm^3\,g^{-1}$), pore size (14.9 nm), particle size distribution clay (1.26%), silts (33.79%), sand (65.23%), soil texture (Sandy loam) CEC (38.65 $cmol^+$/kg), TOC (2.05%) and TKN (0.08%). The soil and composts were sun-dried, crushed to pass through a 1 mm nylon sieve and then manually blended with test soil at an application rate of 50, 150, 250 and 300 kg ha^{-1} of TKN (dry weight basis). Pot specifications and the operational details of the experiments were already reported in our previous study (Wang et al., 2016a). First, the seeds of the Chinese cabbage (*Brassica rapa chinensis* L.) were germinated in petri dishes, and then 10 germinated seeds were sown per pot. Each treatment was triplicate, and this experiment was continued until plant maturity in a greenhouse, with pots placed on a greenhouse bench in a completely randomized block design at an average temperature range of 25–30 °C. When the fourth leaf came out, all pots were thinned and only 5 seedlings were left. The pots were irrigated daily with deionized water to maintain the moisture content to field capacity on an initial weight basis. After 45 days, plants (shoot and root) were harvested, thoroughly washed with tap water, and then rinsed twice with deionized water. Shoots and roots were carefully separated and placed in the paper bags and then oven-dried at 80 °C for 48 h to determine dry weight biomass. Our results provided the total dry weight of biomass.

2.5. Statistical analysis

All of the analyses were performed in triplicate. The data were subjected to one-way analysis of variance (ANOVA) and multiple comparison tests to compare the least significance difference (LSD) at $p = 0.05$ using SPSS v.21 software for windows. Principal component analysis (PCA) was performed using *R* language v3.0 software with the prcomp function and the package ggbiplot, whereas redundancy analyses of physiochemical properties and their correlation during composting was conducted using Canoco 5.

3. Results and discussion

3.1. Evaluation of temperature, cumulative CO_2 emission and electrical conductivity profile during composting

The temperatures monitored from the core of each composting mass through the composting process are shown in Fig. 2a. At the beginning of composting, the temperature in all treatments were in a mesophilic stage (0–72 h), but within a day, the temperature in all 12%B+Z amended treatments rapidly increased and reached a level suited for the thermophiles. For the 12%B added treatment, the temperature reached the thermophilic stage on day 3 and then gradually reduced until the end of composting to reach the ambient level after 14 days. The temperature increased rapidly during the early phase of composting, which indicated the intensive degradation of readily available organic matter. The temperatures were as follows: Z-2, 72 °C; Z-1, 70 °C; B, 65 °C and Z-3, 62 °C. A comparatively lower temperature was observed in the control treatment on day 14, 54 °C. Consequently, no lag phases were observed in the temperature profiles of all biochar (12%B+Z and 12%B alone) amended treatments during the initial 7 days because of the rapid degradation of DFSS. After 14 days, the temperature dropped slowly until the ambient level. This could be explained by the decrease in the availability of readily available organic matter fraction compounds, which were mostly consumed during the thermophilic stage of composting (Zorpas and Loizidou, 2008; Bernal et al., 2009; Zhang et al., 2014; Awasthi et al., 2016a, 2017). A prolonged thermophilic phase was observed in all 12%B+Z amended vessels, which could be due to the faster degradation made possible by the denser composting mixture, such as the addition of biochar filling the pore spaces (Prost et al., 2013; Sun et al., 2016a), A higher dosage of zeolite addition retained the optimum moisture content and porosity (Awasthi et al., 2016a) and thus reduced the heat loss from the composter that occurs because of the greater air space. Moreover, adding biochar combined with zeolite not only led to the rapid uptake of oxygen (Zhang et al., 2014; Awasthi et al., 2016a,b) but also increased the relative abundance of the total microbial population (Karami et al., 2011), which are generally responsible for the faster degradation of more organic material and as a result generate rapid heat during the thermophilic phase of composting. The temperature varied with the amount of zeolite combined with a 12%B, and a similar phenomenon was observed by Sánchez-García et al. (2015) and Awasthi et al. (2017) during the SS composting amended with biochar.

In addition temperature, cumulative carbon dioxide emissions are useful criteria for evaluating the rate of the composting process (Steiner et al., 2010; Czekala et al., 2016), because temperature must be positively correlated with CO_2 emissions and microbial activities (Chen et al., 2010; Awasthi et al., 2016a). The evolutions of cumulative CO_2 emissions in all treatments are compared in Fig. 2b and a considerable correlation between temperature and CO_2 emissions is observed for all the treatments. From the beginning of composting, higher CO_2 emissions were observed for all biochar amended treatments and low CO_2 evolution was observed for the control treatments. This difference could also be explained by the different temperature profiles found for biochar mixed with different concentrations of zeolite compared with only 12%B amended or the control treatment, whereas longer higher temperature profiles were found in all 12%B+Z amended treatments. The

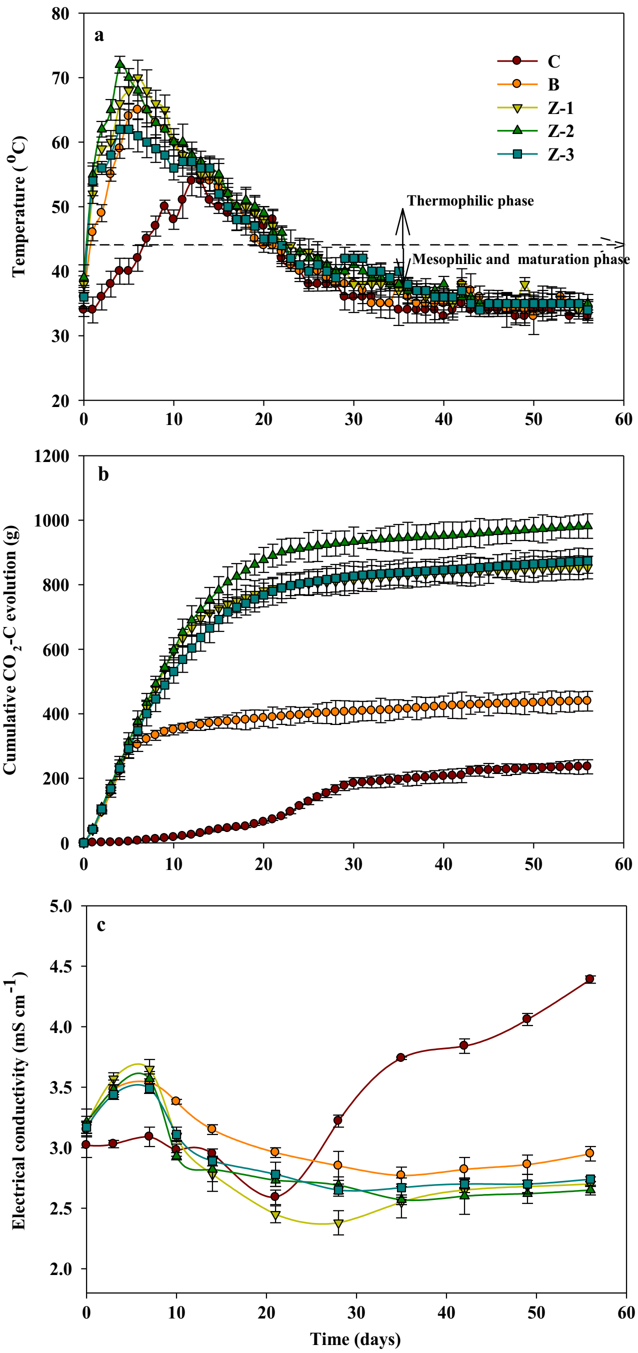

Fig. 2. Evaluation of temperature (a), cumulative carbon dioxide (b) and electrical conductivity (c) in different treatments during composting of dewatered fresh sewage sludge. C: DFSS + WS: Dewatered fresh sewage sludge + wheat straw; B: Dewatered fresh sewage sludge + wheat straw + 12% Biochar; Z-1: Dewatered fresh sewage sludge + wheat straw + 12% Biochar + 10%zeolite; Z-2: Dewatered fresh sewage sludge + wheat straw + 12% Biochar + 15% zeolite; and Z-3: Dewatered fresh sewage sludge + wheat straw + 12% Biochar + 30%zeolite. Results are the mean of three replicates and error bars indicates standard deviation.

maximum cumulative CO_2 was emitted from Z-2 (981.85 g), Z-3 (873.74 g) and Z-1 (853.25 g), whereas considerably very low CO_2 emission was observed for the composting with 12%B or B (438.98 g) and the control treatments (235.68 g). The results indicated that temperature profile in all 12%B+Z amended treatments were considerably higher because the CO_2 emission rate is higher, and collectively both can considered as an indicator of the rate of the composting. The temperature and CO_2 emission profiles were consistent with previous studies, and the underlying reason for the profile shape has been well explained (Dias et al., 2010; Sánchez-García et al., 2015; Awasthi et al., 2016b, 2017).

Electrical conductivity (EC) was closely related to the mineralization of the organic substrate and the concentration of the ionic molecules or mineral fraction (Villaseñor et al., 2011; Sun et al., 2016b). As shown in Fig. 2c, the EC values were 3.15–3.21 ms cm^{-1} and sharply increased (3.54 12%B, 3.65 Z-1, 3.57 Z-2, 3.49 Z-3) in all biochar amended treatments within 7 days, probably because of the mineral salts released and moisture loss by evaporation with the rapid oxidation of complex organic matter (Silva et al., 2009; Awasthi et al., 2017). Thereafter, the EC values gradually decreased in 12%B+ Z and 12%B alone amended treatments, due to the precipitation of ionic molecules and volatilization of extractable ammonium (Fig. 4a). From day 42, the EC value slightly increased in 12%B+Z and 12%B alone until the end of the composting due to the net loss of biomass and the moisture loss not being replaced during the curing phase of composting. In the control, the EC value considerably increased to 3.02–3.09 mS cm^{-1} by day 7, mainly due to the net loss of weight and the release of soluble salts through decomposition activity in the early phase of the composting process. After that, it slightly decreased on day 21, which could be due water loss during the rapid mineralization of OM as reflected in the temperature and CO_2 emission profile (Fig. 2a and b) of the control treatment. Thereafter, the EC values gradually increased until the end of composting, which might due the late of start of the thermophilic phase (Fang and Wong, 1999; Schulz and Glaser, 2012) and because of the precipitation of ionic molecules and volatilization of ammonium not happening. As expected, the addition of 12%B+Z considerably ($P < 0.05$) stabilized the EC values during the composting. The decrease was directly related with the higher dosage of the 12%B+Z. Finally, the treatments of 12%B+Z had lower EC values at the end of the composting process. For example, on day 56, the EC values (mS·cm^{-1}) were 2.74 in Z-3, 2.70 in Z-1, and 2.65 in Z-2, respectively. Thus, the final EC values were within the standard limit of <4.0 mS cm^{-1} considered tolerable for plant growth (TMECC, 2002), and as a result, such composts will not cause any phytotoxicity upon application for organic farming (Biederma and Harpole, 2013). Due to the molecular sieve structure and high cation exchange capacity (CEC) of ~120–160/100 g of zeolite and biochar, it can accommodate and reduce the exchange of positive or negative ionic molecules freely on its surface, adsorb ions (Beesley et al., 2010; Villaseñor et al., 2011; Awasthi et al., 2017) and, as a result, decrease the EC. In contrast, the EC value of the only 12% biochar amended treatment without zeolite was significantly higher (2.82 mS cm^{-1}) after 42, days and the levels were more or less stable in between this value and the end of composting, resulting in an end product within the permissible limit (2.95 mS cm^{-1}). However, some researchers reported that straw biochar amendment increased the water-soluble salts, which led to relatively high concentrations of mineral salts or EC values in the end product (Zorpas and Loizidou, 2008; Zhao et al., 2013; Zhang et al., 2016). Hence, our results revealed that 12%B+Z addition can be considered to be imperative for DFSS composting.

3.2. Evaluation of nutrients transformation profile during composting

3.2.1. Changes in dissolved organic carbon and total organic carbon

DOC is one of the most reliable indicators of biological activities and the rate of composting. During the early or thermophilic phase of composting, the rapid degradation of complex organic compounds in raw feedstock generates smaller and water-soluble molecules, which constitute the dissolved organic fraction or DOC (Prost et al., 2013; Wang et al., 2016a,b) and the concentrations are considerably high. The initial DOC concentrations varied in all the amended treatments due to the addition of a higher dose of biochar in the composting mix. From the beginning of composting, the DOC contents in all 12%B amended composts sharply increased from their levels (g kg^{-1}) in the composting raw materials to those recorded on day 7, from 28.12 to 39.10 in Z-2, 28.17 to 39.51 in Z-3 and on day 14 from 28.14 to 38.96 in Z-1, 27.06 to 35.88 in 12%. In contrast, a considerably low DOC content was observed during the thermophilic phase on day 14, from 25.86 to 28.39, in the control treatment. The corresponding levels (g kg^{-1}) at the end of composting were 10.40 (Z-3), 12.08 (Z-2), 14.27 (Z-1), 15.05 (12%B), and 20.46 (control treatment) (Fig. 3a). Our results are totally different from those of Dias et al. (2010), who reported a continuous DOC decline throughout composting. Meanwhile, it should be noted, that the present study was based on 12% B+Z and 12%B alone, which is completely different from the sawdust or pure biochar used by Dias et al. (2010) in his study. However, control treatment was showed quite similar DOC profile. The DOC concentrations from our study were consistent with those of some previous studies (Chen et al., 2010; Wang et al., 2016b) but were higher than the results reported by Zhang et al. (2016), in which 0.8–1.3 g kg^{-1} of DOC was observed at the end of composting with a 5–15% wheat straw biochar amendment. Consequently, many researchers investigated the relation between the DOC content and compost maturity, and the reduction of DOC concentrations indicated compost stability and quality (Garcia et al., 1991; Huang et al., 2004; Wang et al., 2016a), whereas DOC contents approximately 10 g kg^{-1} for the end product was suggested for matured composts by Zhang et al. (2016). Finally, the relative stability of biochar combined with zeolite resulted in the lowest concentrations of DOC, but it was slightly higher than permissible limit. In the treatments with only 12%B and the control without any amendment, a considerably higher DOC content was observed at the end of experiment, which might be due to slow microbial activities and the late degradation of organic matter because CO_2 emissions and temperature data also support this evidence (Fig. 2).

The TOC content gradually decreased in the composting period among all the treatments, as shown in Fig. 3b. During the bio-oxidative phase (0–14 days), TOC was rapidly decomposed in all biochar amended treatments, mainly due to the mineralization of readily biodegradable TOM by the indigenous microbes and net loss of dry mass in the form of CO_2 emission (Fig. 2b). Once the easily degradable carbohydrates were utilized, complex polysaccharides, such as cellulose, hemicellulose and lignin dominated in the composting mass and became the complex nutrient source for microbial activities; thus the rate of TOC degradation slowed (Awasthi et al., 2016b). The results revealed that minimum TOC after 56 days of composting: 30.07% Z-3, 30.19% Z-2, 30.37% Z-1 and 30.54% 12%B. In contrast, a significantly higher TOC of 37.90% for the control treatment was observed without amendment at the end of composting. The maximum TOC in the control treatment mainly came due to the slow degradation. Similar findings were obtained in previous studies (Silva et al., 2009; Gigliotti et al., 2012; Awasthi et al., 2015, 2016a,b), where the proportion of the bulking agent, mixing of additives and turning frequency of the composting mass were key factors in regulating the TOC degradation during the various types of organic waste composting.

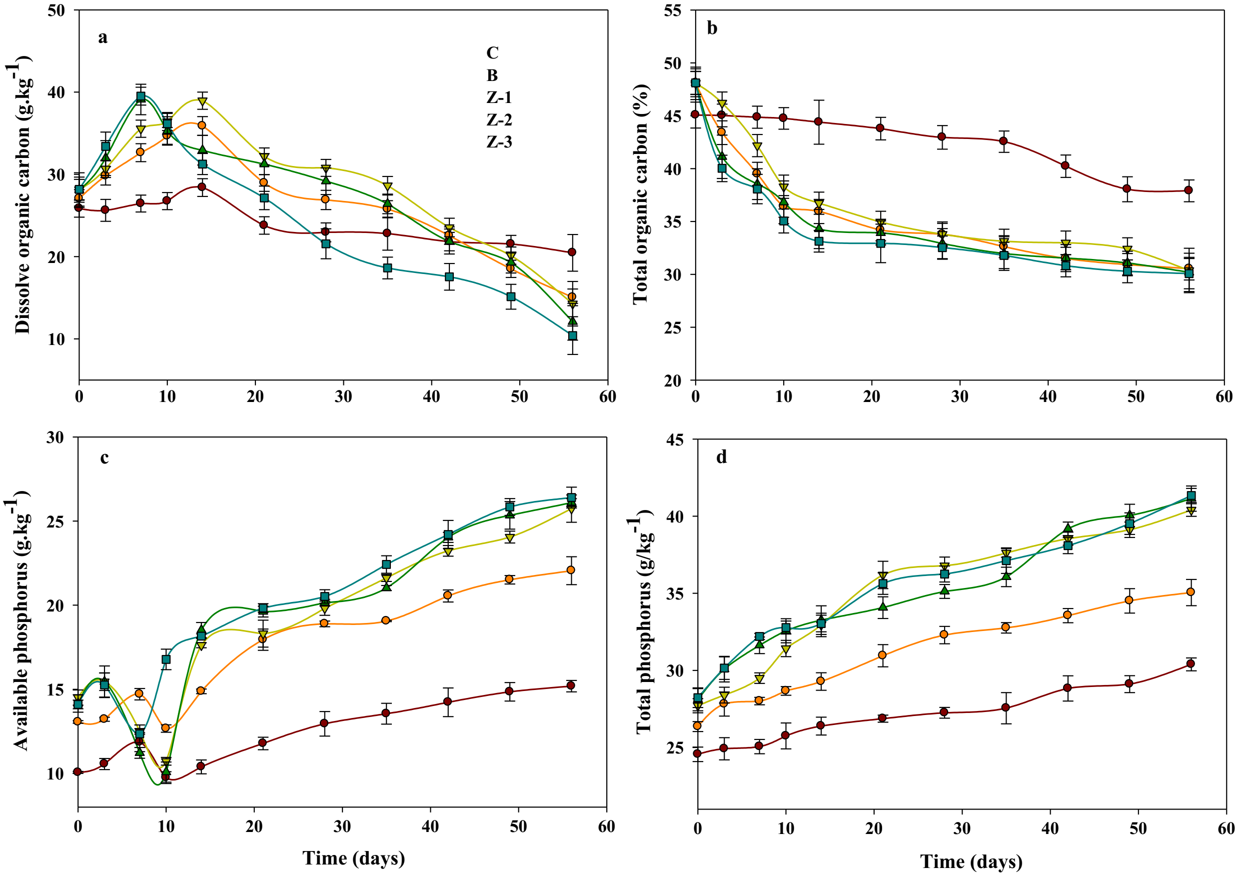

Fig. 3. Evaluation of dissolve organic carbon (a), total organic carbon (b), available phosphorus (c) and total phosphorus (d) in different treatments during composting of dewatered fresh sewage sludge. C: DFSS + WS: Dewatered fresh sewage sludge + wheat straw; B: Dewatered fresh sewage sludge + wheat straw + 12% Biochar; Z-1: Dewatered fresh sewage sludge + wheat straw + 12% Biochar + 10% zeolite; Z-2: Dewatered fresh sewage sludge + wheat straw + 12% Biochar + 15% zeolite; and Z-3: Dewatered fresh sewage sludge + wheat straw + 12% Biochar + 30% zeolite. Results are the mean of three replicates and error bars indicates standard deviation.

3.2.2. Changes in DON, NH_4^+-N, NO_3^--N, TKN, AP and total phosphorus

The variation in the concentrations of DON, NH_4^+-N, NO_3^--N and TKN throughout DFSS composting is presented in Fig. 4. The concentration of DON slightly increased on day 3 and then sharply decreased on day 14. Thereafter, it gradually increased in all the treatments until the end of composting. The corresponding increasing trends for the all treatments (mg kg^{-1}) were as follows: Z-2, 72.9 to 1582; Z-1, 72.4 to 1423; Z-3, 70.1 to 1409; 12%B, 65.4 to 1251 and 45.2 to 682.5 for the control. The DON content increased during the early stage of composting, due to the rapid mineralization of complex insoluble polymers such as protein, nucleic acid and mass losses (Li et al., 2012; Zhang et al., 2016). During the first 7 days, the NH_4^+-N content peaked in the 12%B +30%Z and only 12%B treatments. In the 12%B+10%Z and 12%B +15%Z amended treatments, the maximum NH_4^+-N content was observed on day 10, whereas in the control treatment, the maximum NH_4^+-N content was observed on day 28. The NH_4^+-N profiles were consistent with previous studies, and the underlying reason for the profile shape has been well explained (Huang et al., 2004; Sánchez-García et al., 2015; Zhang et al., 2016; Awasthi et al., 2016a). However, our results are quite similar to those obtained by Zhang et al. (2016), who investigated changes in biological properties of the compost made from a pig manure mixed with wheat straw biochar and observed that the production of volatile fatty acids considerably decreased the concentration of NH_4^+-N and showed no immediate effect on temperature and CO_2 profile. The increase in the NH_4^+-N concentration was due to simultaneous ammonification, increased temperature and pH (data not shown), and rapid mineralization of organic nitrogen compounds. In addition, neither the DON content nor the NH_4^+-N concentration had any considerable influence on the TKN content (Fig. 4d), which increased in all biochar amended treatments as a consequence of the net loss of dry matter in terms of carbon dioxide, whereas the concentration of TKN in the control treatment was drastically lower than that in all biochar amended treatments, which could be a low decomposition or a higher loss of ammonia (Dias et al., 2010; Huang et al., 2004; Gigliotti et al., 2012; Awasthi et al., 2016b). After the thermophilic phase, the amounts of NH_4^+-N were gradually decreased in all biochar amended treatments until the end of composting, which might be due to the conversion of NH_4^+-N into NH_3 (data not shown) and subsequently by its volatilization under high pH (data not shown) and temperature conditions. All biochar amended treatments showed good mineralization of nitrogenous compounds (Fig. 4c); however, the maximum NH_4^+-N concentrations of treatments 12%B combined with 10% (Z-1), 15% (Z-2) and 30% (Z-3) zeolite were considerably higher than the treatment of only 12%B because some ammonium ions might be precipitated with zeolite. Comparing the NH_4^+-N concentration with the control, the NH_4^+-N concentrations increased gradually until day 35 and the concentration was considerably above the permissible limit after day 56 of composting (TMECC, 2002), which is mainly due to the delayed organic matter mineralization and thermophilic phase (Fig. 2a). Biochar mixed with a higher dosage of zeolite amendments have the potential to reduce the

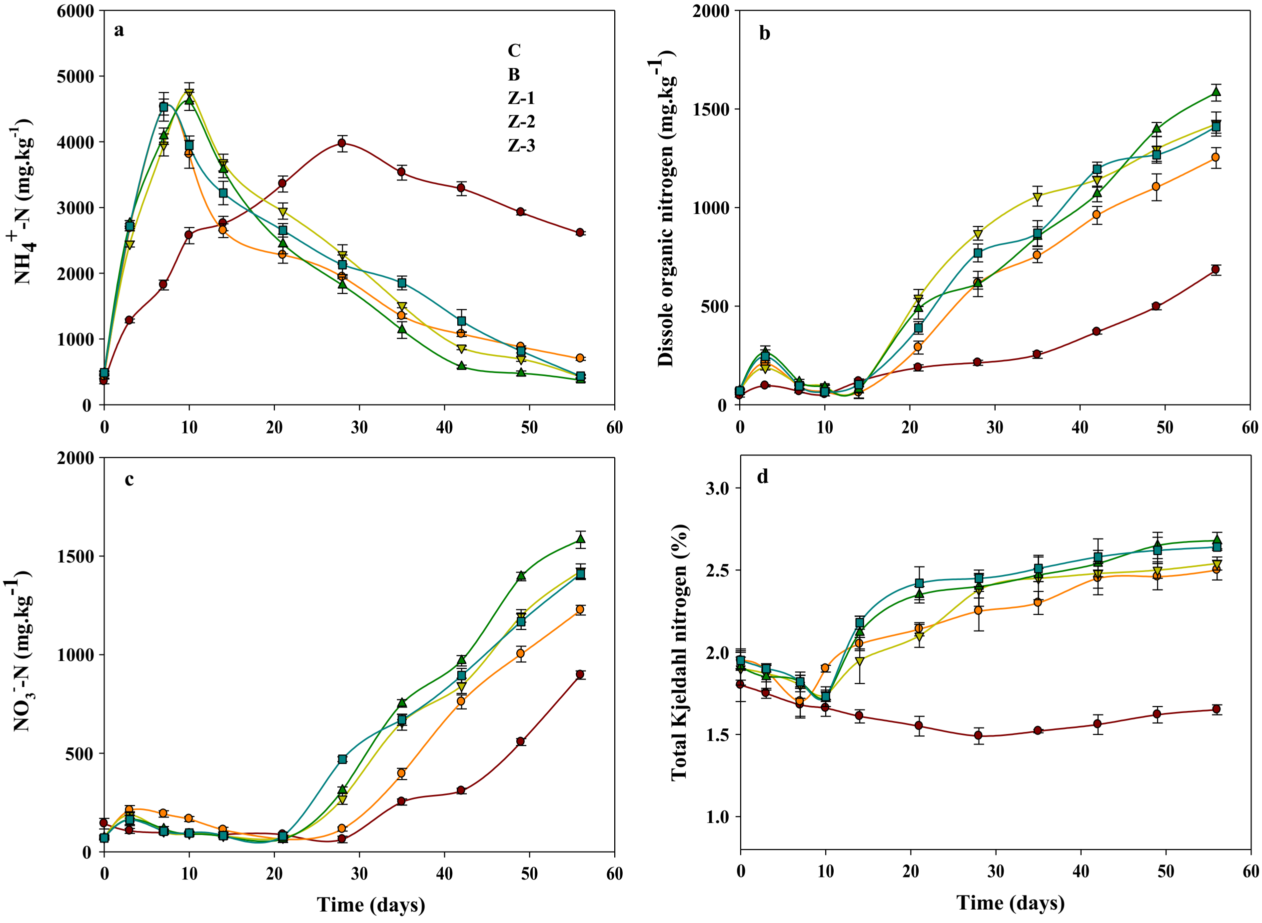

Fig. 4. Evaluation of extractable ammonium (a), dissolve organic nitrogen (b), nitrate (c) and total Kjeldahl nitrogen (d) in different treatments during composting of dewatered fresh sewage sludge. C: DFSS + WS: Dewatered fresh sewage sludge + wheat straw; B: Dewatered fresh sewage sludge + wheat straw + 12% Biochar; Z-1: Dewatered fresh sewage sludge + wheat straw + 12% Biochar + 10% zeolite; Z-2: Dewatered fresh sewage sludge + wheat straw + 12% Biochar + 15% zeolite; and Z-3: Dewatered fresh sewage sludge + wheat straw + 12% Biochar + 30% zeolite. Results are the mean of three replicates and error bars indicates standard deviation.

volatilization of NH_4^+-N during composting mostly because of three factors. (1) The excellent sorption/adsorption capacity of for ionic molecules (because of its porous structure, small surface area and dominance of micro-pores) leads to more ammonia being absorbed, which means less NH_4^+-N is available during composting (Hua et al., 2009; Malinska et al., 2014; Zhang et al., 2016; Awasthi et al., 2016b). In the previous investigation, the addition of 12%B+Z considerably reduced the ammonium and GHGs during SS composting (Awasthi et al., 2017). (2) Biochar mixed with zeolite provides a favorable environment condition for nitrifying bacteria that converting ammonia (data not shown) to nitrate, which means that biochar-treated compost is richer in nitrogen (Zhang et al., 2014; Zhang et al., 2016). (3) Biochar and zeolite absorb larger quantities of ammonia (data not shown) with the rapid mineralization of organic matter during SS composting (Zorpas and Loizidou, 2008; Malinska et al., 2014; Awasthi et al., 2017). At the beginning of composting, the nitrate content was considerably low in all treatments (Fig. 4c), but as the mineralization of nitrogenous organic matter started, the nitrate contents slightly increased on day 3 and then gradually decreased on day 21 in all biochar amended treatments and on day 28 in the control treatment, which could be because biochar has a higher nitrate adsorption capacity (Beesley et al., 2010; Zhang et al., 2014). When compared to the control treatment, the biochar amended treatments had lower NH_4^+-N and higher nitrate contents at the end of composting. 12% B+Z and only 12%B led to a more favorable micro-environment for the indigenous nitrifying bacteria. In addition, Dias et al. (2010) used the nitrification index (NH_4^+-N/NO_3^--N ratio) to measure the maturity of compost and suggested that a value below 0.5 indicated fully mature compost and a value from 0.5 to 3.0 indicated mature compost, and a value above 3.0 indicated immature compost. Finally, the nitrification index values on day 56 of SS composting were as follows: 3.20 in the control, 0.48 in 12%B alone, 0.28 in Z-1, 0.23 in Z-2, and 0.30 in Z-3. Thus, at the end of composting, the nitrification index contents in all biochar combined with zeolite amended treatments were considerably lower than the standard limit for compost application and indicated that the final product of the treatments with 12% B+15% Z was the most mature of the treatments. Meanwhile, the results of previous studies were in line with our present investigation (Jindo et al., 2012; Malinska et al., 2014; Zhang et al., 2016).

As shown in Fig. 3c, the AP content in all the treatments initially slightly increased, then decreased and finally increased with the composting process, whereas the AP values among the all treatments began increasing from the day 14 and then kept increasing until the end. The considerable loss of AP was probably due to the rapid degradation of organic phosphorus and utilization by microorganisms (Biederman and Harpole, 2013). The AP concentration was 28–32% higher in all biochar amended treatments compared to the control at the end of composting. Consequently, the TP contents in all the treatments showed an increasing trend with an extended composting period (Fig. 3d), which could be attributed to the enrichment effect of the degradation of organic matter. This result is observed because biochar combined with zeolite amendment has a maximum AP and TP content than 12%B alone applied treatment, whereas there is very low AP and TP content in control treatment. Our results support the previous studies of Chen et al. (2010), Li et al. (2012), Wang et al. (2016b), and Zhang et al. (2016), who observed the influence of bamboo charcoal, Ca-bentonite and wheat straw biochar amendments on water-soluble phosphorus and the TP content for pig manure composting.

3.2.3. Changes in W-Na^+, W-K^+, T-Na and T-K

The concentration of water-soluble (W-Na^+ and W-K^+) and total Na^+ and K^+ (T-Na^+ and T-K^+) in all biochar added treatments was more are less similar throughout the composting process (Fig. 5). The W-Na^+ and W-K^+ contents in all biochar amended treatments were increased until day 3, whereas W-Na^+ decreased from day 7 to 28 and W-K^+ decreased from day 7 to 21, and then gradually increased again until the end of the composting. In the control, the trend of both W-Na^+ and WK^+ contents were totally different, which could be due to the lower decomposition and the low pH (data not shown) not allowing further transformation of total organic nutrients (T-Na^+ and T-K^+); W-Na^+ and W-K^+ might also be affected. A similar trend was also observed by Zhang et al. (2016) for pig manure composting amended with wheat straw biochar. On day 56 of DFSS composting, the concentration (g kg^{-1}) of W-Na^+ was 3.71 in Z-2, 3.56 in Z-1, 3.42 in Z-3, 3.25 in the only 12% B treatment and 2.40 in control treatment; and these results indicate that addition of biochar increased the concentration of water-soluble Na^+ by 50–60% compared to the control. The concentration of W-K^+ (g kg^{-1}) was 2.43 in the control, 3.30 in 12%B, 4.29 in Z-1, 4.62 in Z-2 and 3.97 in Z-3, whereas the overall increase in all biochar amended treatments than the control being 52–56%. Overall, the treatments amended with biochar combined with zeolite had a higher concentration of W-Na^+ and W-K^+ during the whole experimental period compared to the control and 12%B amendment, demonstrating an efficient influence of zeolite for the rapid degradation of complex organic matter, and the temperature and the CO_2 emission profile also support this evidence (Fig. 2). In the control treatment, water-soluble Na^+ and K^+ had a considerably low content, which might be due to an acidic condition not favorable for rapid mineralization, and then the T-Na^+ and T-K^+ could not be transformed into water-soluble ions. Meanwhile, a growing concern associated with compost application is that crops or plants take up cations in the form of W-Na^+ and W-K^+ from the soil and need to adsorb a similar quantity of water soluble anions to remain neutral, with PO_4^{3-} or AP being the preferred anion.

However, treatments of biochar combined with zeolite have higher concentrations of Na^+ compared to the control, but its concentration is within the standard limit ($\leq$ 4% dw) of TMECC (2002) because excessive levels of Na^+ could lead to a poor soil structure and affect plant growth (Sánchez-García et al., 2015; Zhang et al., 2016). In addition, wheat straw biochar has its own physicochemical characteristics and provides a favorable condition for indigenous microorganisms. Consequently, 12% biochar combined with a higher dosage of zeolite reduced the compactness of composting feed-stocks and increased the availability of oxygen, which were collectively support to increased the rate of organic matter degradation (Liu et al., 2011; Awasthi et al., 2016a). The 12%B+Z amendment increased the TOM degradation when it was composted mixed with DFSS and wheat straw. Simultaneously, the wheat-straw biochar was rich in nutrients than zeolite, which considerably leading to the enrichment of the compost and increasing its agronomic value. Furthermore, the micro-porous surface charge of biochar and zeolite increased the capacity for exchange with cations and anions in the compost and allowed the retention of nutrients (Jindo et al., 2012; Villaseñor et al., 2011; Zhang et al., 2016). All of these factors might have a synergistic impact and improve the soil properties, plant growth, total biomass and crop yield after the application of B+Z amended compost to soil. However, many previous studies reported that biochar does not alter the soil nutrient environment better than chemical fertilizers; while some previous studies prove that the amendment of biochar is much more effective than chemical fertilizers to increased the concentrations of Na, K and P in plant tissue (Karami et al., 2011; Biederman and Harpole, 2013; Zhang et al., 2016; Awasthi et al., 2017).

3.2.4. Changes in soluble and total C/N ratio

Carbon and nitrogen are two important nutrients mainly used by indigenous microorganisms for energy production and cell

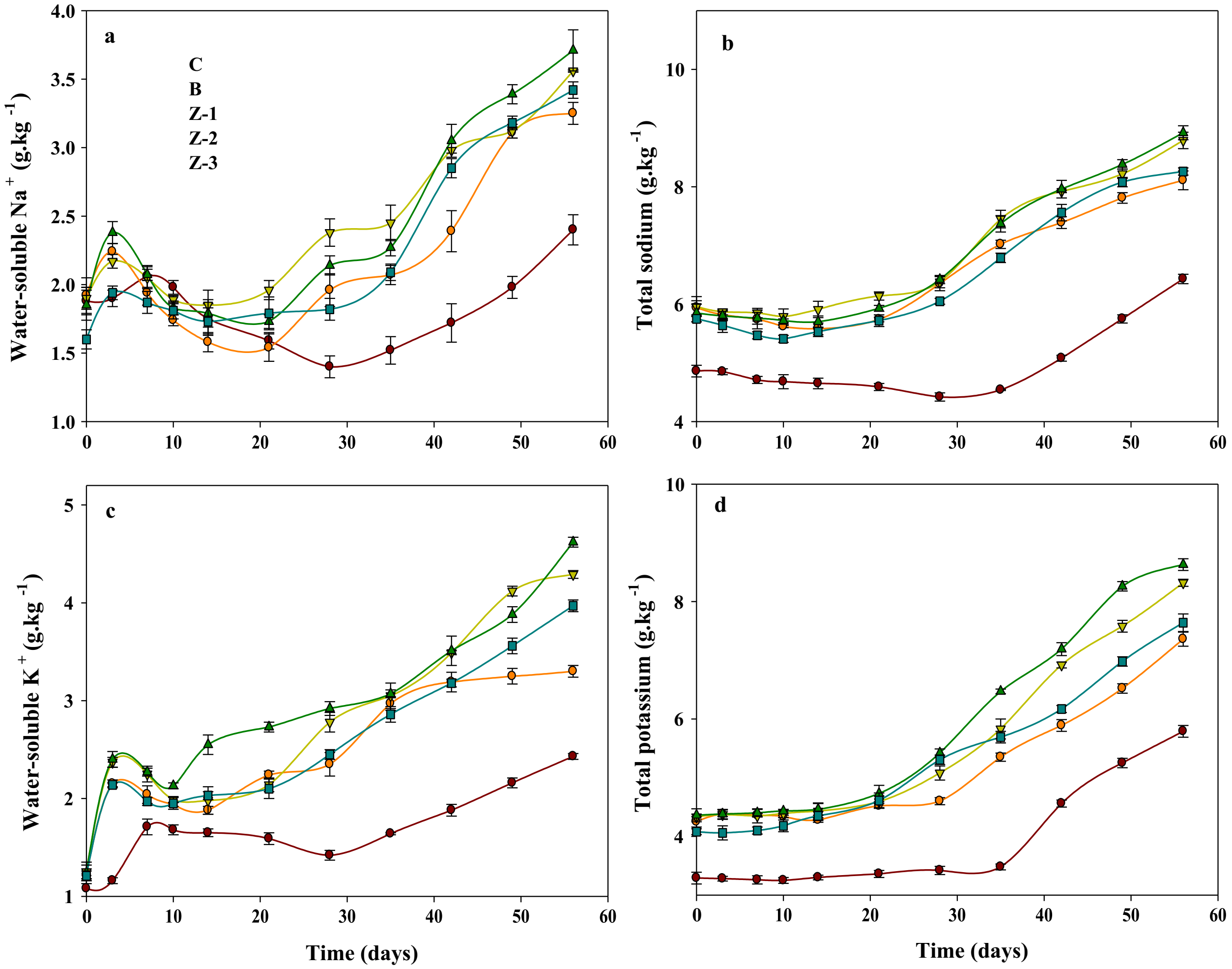

Fig. 5. Evaluation of water soluble sodium (a), total sodium (b), water soluble potassium (c) and total potassium (d) different treatments during composting of dewatered fresh sewage sludge. C: DFSS + WS: Dewatered fresh sewage sludge + wheat straw; B: Dewatered fresh sewage sludge + wheat straw + 12% Biochar; Z-1: Dewatered fresh sewage sludge + wheat straw + 12% Biochar + 10% zeolite; Z-2: Dewatered fresh sewage sludge + wheat straw + 12% Biochar + 15% zeolite; and Z-3: Dewatered fresh sewage sludge + wheat straw + 12% Biochar + 30% zeolite. Results are the mean of three replicates and error bars indicates standard deviation.

growth during composting, which results in considerable variation in the C/N ratio, which is widely used to assess the end product maturity. As shown in Fig. 6, the soluble C/N ratio initially slightly decreased, then increased and finally gradually decreased in all treatments, whereas the solid C/N ratio gradually decreased until the end of composting in all treatments. At the end of composting, the lowest C/N ratios in terms of both solid and soluble fractions were observed in the Z-3 or 12%B+30%Z added treatment. Comparatively higher C/N values were observed in the control treatment with a solid C/N ratio of 22.96 and soluble C/N ratio 0.03 at the end of composting, which are higher than permissible limits. The increasing or decreasing trend of the C/N ratios with composting time was probably due either to the rapid mineralization of the complex organic substrate or to the increase in total nitrogen following the loss of carbon in the form of CO_2 (Huang et al., 2004; Awasthi et al., 2015; Zhang et al., 2016). The C/N ratio can be used as an indicator for compost stability because composting involves biochemical reactions occurring mainly in the aqueous phase. Several authors indicate that a soluble C/N ratio of 5–6 and solid C/N ratio of less than 20 are considered as satisfactory levels for maturity (TMECC, 2002); thus the final soluble C/N and solid C/N ratio of all biochar amended treatments in this study met the requirements of compost maturity stipulated for organic manures, whereas the solid C/N ratio in the control treatments was above the permissible limit at the end of composting, perhaps due to slow degradation. The reduction of the total carbon content but increase in the total nitrogen content resulted in a decrease in the C/N ratio during composting, indicating that the composts were becoming stable and mature. These results were in line with the several earlier researchers (Zorpas and Loizidou, 2008; Awasthi et al., 2017) who reported that the C/N ratio gradually declined with the composting period; Zhang et al. (2016) obtained similar results for the composting of pig manure amended with wheat straw biochar that had been pyrolyzed at 500–600 °C.

3.3. Correlation analysis

According to the principal component and redundancy analysis of the physiochemical changes, which is listed in Fig 7, there is a statistically significant correlation ($P < 0.05$) between nutrient transformation and temperature as well as carbon dioxide emission in all biochar added treatments. Meanwhile, the samples taken during the maturation of all biochar amended treatments showed the greatest dispersion along the axes. The 12%B+Z and only 12% B amendments were responsible for the differences between physiochemical parameters along principal component one (PC1), differentiating samples during the maturation of B+Z, only 12%B and without an amendment or the control treatment

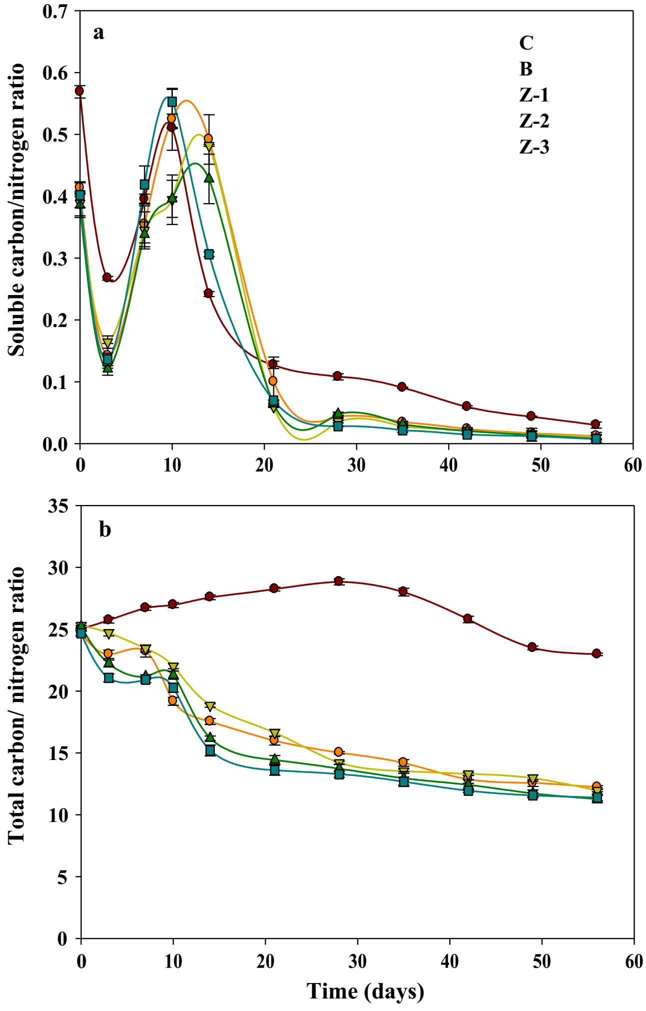

Fig. 6. Evaluation of soluble carbon/ nitrogen ratio (a) and total carbon/ nitrogen ratio (b) different treatments during composting of dewatered fresh sewage sludge. C: DFSS + WS: Dewatered fresh sewage sludge + wheat straw; B: Dewatered fresh sewage sludge + wheat straw + 12% Biochar; Z-1: Dewatered fresh sewage sludge + wheat straw + 12% Biochar + 10%zeolite; Z-2: Dewatered fresh sewage sludge + wheat straw + 12% Biochar + 15% zeolite; and Z-3: Dewatered fresh sewage sludge + wheat straw + 12% Biochar + 30% zeolite. Results are the mean of three replicates and error bars indicates standard deviation.

(Fig. 7a). During the process, 12%B+15%Z maintained a high concentration of water soluble macro-nutrients nutrients at the beginning of composting and minimum during the maturation phase. Both 12%B and B+Z amended treatments reached maximum nutrient contents during the thermophilic phase, and then dropped throughout the maturation process to achieve within the standard value at the end of composting (Table 3). In terms of carbon dioxide and temperature, all biochar added treatments remained considerably higher at the beginning of the composting process, whereas the control treatment showed very low CO_2 emissions and temperatures during the first seven weeks, obtaining minimum water-soluble macro-nutrients by day 21 and immature compost by day 56 at the end of the process. However, the physicochemical parameter with the largest contribution to the mineralization of organic matter is along principal component two (PC2), with the trend of soluble and total C/N ratio ($r = 0.98$, $p < 0.0001$), primarily differentiating between all B+Z and 12%B added and the control treatments (Fig. 7a). At the end of composting, C/N > 23.0 in the control treatment, which was considerably higher than the values of all biochar amended treatments, which were approximately 11.3–12.2, which are considerably within the permissible value of standards for organic farming of compost (Table 3). Consequently, the level of maturity is positively correlated with respiration activity in the evaluated composts, especially in the B+Z amended treatments. Similar results were observed by Zhao et al. (2013) in the composting of chicken feathers and Villar et al. (2016) during the composting of SS. Both temperature and CO_2 emissions showed compost stability and presented considerable correlation with nutrient transformation. Because a positive considerable correlation between CO_2 emission variations and the temperature profile was observed, they were suitable for estimating the activities of microorganisms during DFSS composting processes with a higher dosage of 12%B+Z added treatments. High TOC mineralization and CO_2 emissions correspond to when high amendment ratios of Z-2 or 12%B+15%Z are used as additives, which is consistent with results observed by Sun et al. (2016a) and Zhang et al. (2014). Water-soluble nutrients were also positively correlated with CO_2 emissions and the temperature profile, especially in the all 12%B+Z mixtures. In the present investigation, CO_2 emissions showed considerable correlations with the temperature and maturity parameters with the composting process (Table 3). A high correlation among CO_2 emissions and water-soluble nutrients, total nutrients and temperature in the 12%B+15%Z amended treatment led to the conclusion that these maturity parameters could be suitable indicators for the formulation of a novel feed stock and the advancement of the composting process and the stabilization of TOM during DFSS composting.

3.4. The quality of the end products

The physical properties and nutrient contents in the composts are important indicators for evaluating the quality of DFSS compost when being used as organic fertilizers or soil amendments (Silva et al., 2009; Awasthi et al., 2016b, 2017). Table 3 shows that the pH values, TOM, water soluble (AP, W-Na^+, W-K^+, and soluble C/N ratio) and total nutrient content (TP, T-Na, T-K, and TKN) in all biochar amended treatments at the end of composting met the desired limitations of the compost as per organic fertilizer standards (TMECC, 2002). The nutrient content in all B+Z added treatments were significantly higher ($p < 0.05$) than in the only 12%B and without amended treatments or the control treatment (Table 3). However, in the control treatment compost, some nutrient contents were within the permissible limit, but the seed germination index and CO_2 respiration indicate that this compost was not properly stabilized and mature for organic farming. Meanwhile, the above results showed that the combined addition of biochar and zeolite and mainly the 12%B+15%Z and Z-2 treatments, which resulted in a higher concentration of nutrients in the end product, might be one possible reason the biochar combined with zeolite increased the microbial activities and as a consequence enhanced the degradation of DFSS, which would increase the water-soluble and total nutrients. In addition, biochar itself contains a substantial amount of macro and micro-nutrients, which are mineralized and add to the total nutrient content of compost (Zorpas and Loizidou, 2008; Zhang et al., 2014; Awasthi et al., 2016a,b).

In addition, the evolution rate of the amount of CO_2 of the final compost derived from all biochar amended treatments were within the standard value of 2–4 g °C $(gVS)^{-1}$ day^{-1} (TMECC, 2002; CCME, 2005), and our results clearly indicated that the biochar amended compost was fully stabilized after 35 days of composting. The above result shows that the combined addition of 12%B+Z in the DFSS composting process not only reduces the composting time but also enhances the organic matter mineralization and the quality and stability of the end product. It has been

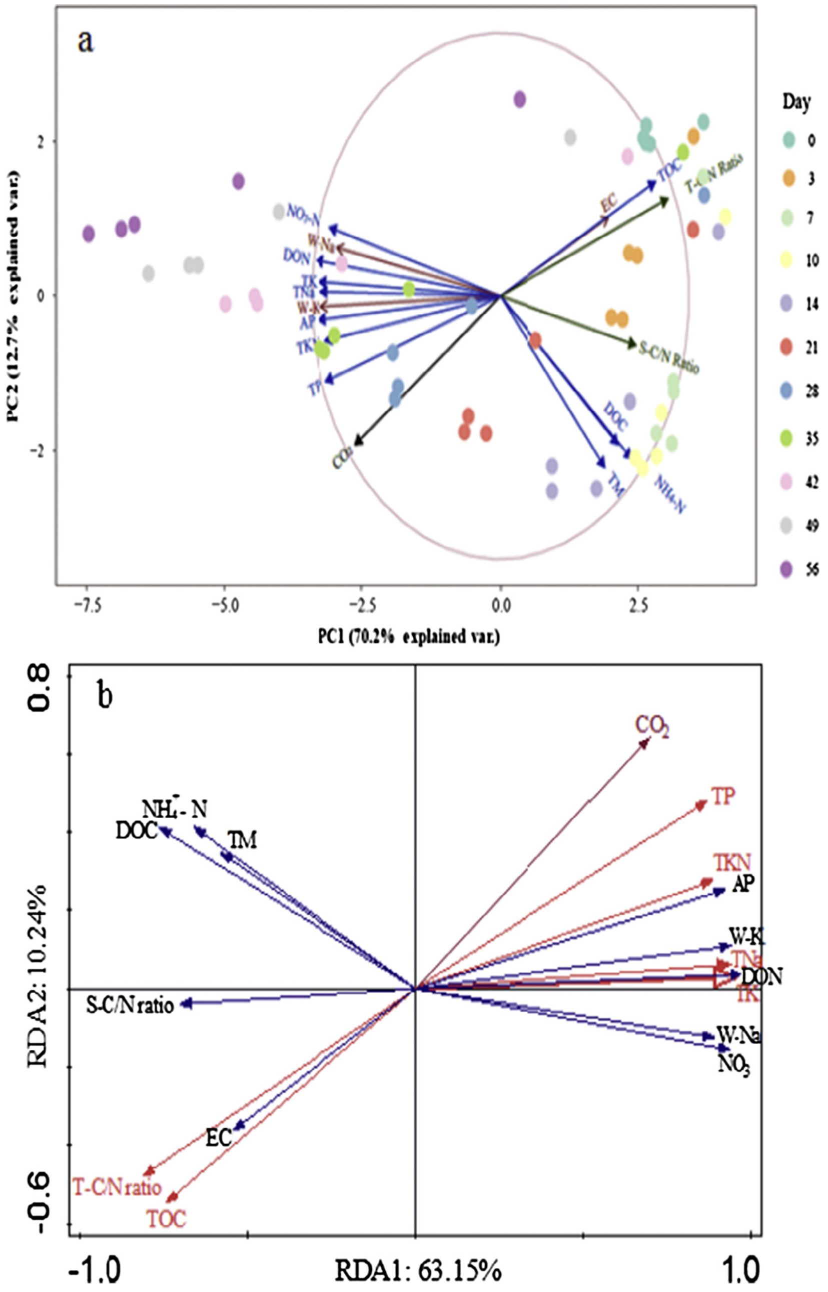

Fig. 7. (a) Correlation biplot of principal component analysis where vectors correspond to the variables that define the treatments and points correspond to sampling during the composting of dewatered fresh sewage sludge, (b) Redundancy analysis (RDA) of physiochemical properties and nutrient transformation during the composting. The correlation between physiochemical properties and nutrient transformation can be approximated by a perpendicular projection of the three different color variable arrow-tips onto the line overlaying the ordination axes. The length of the physiochemical properties arrows is the multiple correlations of that studied nutrient transformation with the ordination axes.

Table 2
Selected physicochemical properties of composting materials used in the present experiments (dry weight basis).

Parameters	Moisture content (%)	pH	Total organic carbon (%)	Total Kjeldahl nitrogen (%)	C:N ratio
DFSS	82.78 ± 2.45	7.43 ± 0.02	42.84 ± 1.20	3.05 ± 0.11	14.0 ± 0.1
WS	12.59 ± 0.57	4.18 ± 0.03	61.27 ± 1.03	0.88 ± 0.04	69.6 ± 0.1
Mix	55.40 ± 3.34	7.62 ± 0.05	45.06 ± 2.08	1.80 ± 0.03	25.03 ± 0.20
Zeolite	0.06 ± 0.01	8.10 ± 0.04	ND	ND	ND
Biochar	4.18 ± 0.10	8.84 ± 0.06	67.79 ± 1.15	0.62 ± 0.06	109.3 ± 2.0

ND (Not detected), DFSS (dewatered fresh sewage sludge) and WS (Wheat straw). Results are the mean of three replicates ± standard deviation.

Table 3
Selected compost maturity parameters at the end of dewatered fresh sewage sludge composting (dry weight basis).

Parameters	C	B	Z-1	Z-2	Z-3	TMECC (2002), CCME (2005)
pH	5.06 ± 0.02	7.15 ± 0.04	7.42 ± 0.03	7.86 ± 0.05	7.78 ± 0.06	5.5–8.5
Electrical conductivity (mS· cm^{-1})	4.39 ± 0.03	2.95 ± 0.06	2.70 ± 0.02	2.65 ± 0.03	2.74 ± 0.02	≤ 4
CO_2 evolution rate (g C (kg VS)$^{-1}$ day^{-1})	8.25 ± 1.36	1.79 ± 0.05	1.88 ± 0.03	1.14 ± 0.04	1.05 ± 0.02	2–4
Ammonium (mg/kg^{-1} dw)	2608 ± 5	698.1 ± 4.36	423.7 ± 2.8	372.1 ± 3.14	434.2 ± 2.1	75–500
Total organic matter (%)	86.46 ± 1.07	68.10 ± 1.54	38.04 ± 2.17	33.46 ± 1.04	35.19 ± 1.08	≥ 40
Total organic carbon (%)	37.90 ± 1.03	30.54 ± 1.07	30.37 ± 2.10	30.19 ± 1.81	30.07 ± 1.43	–
TKN (%)	1.65 ± 0.02	2.50 ± 0.06	2.54 ± 0.04	2.68 ± 0.05	2.64 ± 0.02	–
C:N ratio	23.0 ± 0.1	12.2 ± 0.3	12.0 ± 0.1	11.3 ± 0.2	11.4 ± 0.1	≤ 25
Total N:P: K	12.61 ± 0.08	14.97 ± 0.05	17.03 ± 0.07	17.61 ± 0.12	17.20 ± 0.06	–
Seed germination index (%)	45.85 ± 2.78	97.20 ± 6.79	110.5 ± 5.2	127.8 ± 4.1	104.1 ± 5.1	80–90

C: Dewatered fresh sewage sludge + wheat straw (Control); B: Dewatered fresh sewage sludge + wheat straw + 12% biochar; Z-1:Dewatered fresh sewage sludge + wheat straw + 12% biochar + 10% zeolite; Z-2: Dewatered fresh sewage sludge + wheat straw + 12% biochar + 15% zeolite; and Z-3: Dewatered fresh sewage sludge + wheat straw + 12% biochar + 30% zeolite. Results are the mean of three replicates ± standard deviation; ND-Not detected.

recognized that the TOM in compost must be well stabilized before the compost is applied to soil; otherwise, it can have a toxic effect on plants because of the depletion of oxygen in plant roots due to the competition for oxygen between the microbial biomass and plant roots (Gigliotti et al., 2012). The degree of stability and maturity of compost are the most important factors affecting its successful application for agricultural purposes (Beesley et al., 2010). Therefore, stabilization and maturity are used as quality criteria for compost products (Zhang et al., 2016). Because maturation not only depends on the physiochemical properties but also implies the degree of OM humification, the amount of CO_2 generally released by the final compost also serves as a criterion of the maturity. The above results showed that high quality composts can be obtained by composting of DFSS mixed with a higher dosage of 12%B+Z as additives. However, due to the differences in the dosage of the zeolite, the composts are different in their properties and therefore have different effects when applied to soils. Among all the biochar amended composts, the compost with 12%B+15%Z has the highest contents of soluble and total nutrients and GI as well as lower CO_2 evolution values at the end of composting; therefore, it can be considered a good soil amendment for improving the soil texture and nutrient contents. The compost with 12%B+15%Z has a higher content of total N:P:K and is an excellent organic fertilizer in supplementing deficiencies of N:P:K in soil; consequently, the compost with a pH >7.50 improves soil acidity.

3.5. Chinese cabbage biomass response to matured compost

Fig. 8 presents the influence of well-matured compost on the biomass production of *B. rapa* L. The addition of biochar amended composts significantly increased ($P \leq 0.01$) biomass compared to the control treatment, but the addition of 150 kg ha^{-1} TKN showed the maximum biomass. Different dosages of TKN showed disparate effects on the biomass. The highest biomass was obtained from the 150 kg ha^{-1} TKN, which was obtained with the 12%B+15%Z amended compost. The biomass was 85% higher compared to the control, followed by 12%B+10%Z at 74%. The addition of 12%B alone and 12%B+30%Z at an application dose of 50 kg ha^{-1} TKN and 250 kg ha^{-1} TKN also significantly ($P \leq 0.05$) increased the yield, by 45 and 39%, respectively (Fig. 8). The 12%B+15%Z amended treatment compost at 150 kg ha^{-1} TKN increased the availability of macro-nutrients in soils to levels that can improve the growth of Chinese cabbage and its biomass. Further, the 12%B+15%Z amended treatment compost at 150 kg ha^{-1} TKN seems to have reduced the availability of heavy metals, because biochar and zeolite both have an excellent ability to immobilize the heavy metals and reduce the bioavailability for plants. The maximum biomass was obtained from 12%B+15%Z or Z-2 and 12%B+10%Z or Z-1 at 150 kg ha^{-1} TKN amendments; the underlying reason for the profile shape has been well explained in previous studies (Biederman and Harpole, 2013; Sun et al., 2016a). The results of the present experiment are consistent with previous findings reporting that biochar and additives such as Ca-bentonite amended compost reduced the bioavailability of HMs concentrations in contaminated soils (Khan et al., 2015; Wang et al., 2016a). In our previous research, we also reported that biochar amended compost and some other additives (CaO, fly ash, sulfur and Na_2S) considerably reduced the bio-accessibility of Cu, Cd, Pb and Zn in soil for the growth of Chinese cabbage and ryegrass (Li et al., 2015; Biederman and Harpole, 2013). Reduced bio-available HMs concentrations are not applicable to all types of soils and biochar or additive amended composts. The mechanisms accounting for the reduced HMs bio-accessibility in 12%B+Z or biochar amended compost is connected to changes in the pH, DOC and cation exchange properties of the amended soil (Méndez et al., 2012; Khan et al., 2015).

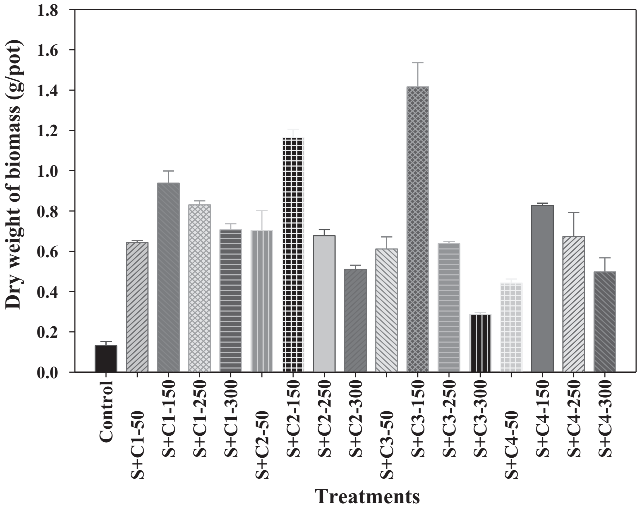

Fig. 8. Effect of biochar amended compost on Chinese cabbage seedling growth in green house pot experiment. Soil- blank treatment, Soil- Control, 50–50 kg ha^{-1} total Kjeldahl nitrogen compost mixed with soil, 150–150 kg ha^{-1} total Kjeldahl nitrogen compost mixed with soil, 250–250 kg ha^{-1} total Kjeldahl nitrogen compost mixed with soil, and 300–300 kg ha^{-1} total Kjeldahl nitrogen compost mixed with soil. S + C1: Soil mixed with compost (12% biochar amended compost), S + C2: Soil mixed with compost (12%biochar + 10% zeolite amended compost), S + C3: Soil mixed with compost (12% biochar + 15% zeolite amended compost) and S + C4: Soil mixed with compost (12% biochar + 30% zeolite amended compost). Results are the mean of three replicates and error bars indicates standard deviation of triplicates.

Meanwhile, the end product of the 12%B+15%Z and 12%B+10%Z amended treatment contained the maximum NO_3^--N and DON (Fig. 4) and the lowest NH_4^+-N among the other biochar amended treatments' compost, which should also lead to higher yields or biomass of Chinese cabbage; however, only the 12%B amended compost had among the highest NH_4^+-N and lowest NO_3^--N and DON concentration, indicating that other factors, such as the addition 12%B+Z, could have affected growth [e.g., aeration, as 12%B+Z amended compost has the largest pore volume and pore size as well as heavy metals immobilization (Table 3)]. 12%B+Z amendments have caused both considerable and non- considerable increased in plant biomasses, but the effect depends on the bioavailability of macro- and micro-nutrients, which has sometimes also been related to the level of toxicity, but the causes are not always clear (Beesley et al., 2010; Karami et al., 2011). Finally, the results indicated that compost at an application rate of 150 kg ha^{-1} TKN (dry weight basis) could improve the yield of Chinese cabbage based on our pot experiment, but for field application, the amount could be too high. Therefore, a field scale experiment is warranted to confirm the compost's application rate.

4. Conclusions

This work has demonstrated that the combined use of 12%B+Z has a positive effect for DFSS composting, which could considerably increase the water-soluble nutrients compared to only 12%B and control treatments. Further, the addition of 12%B+15%Z adequately increased the organic matter mineralization and showed higher water-soluble and total macro-nutrients during composting. The results indicated that the amendment of 12%B+15%Z could facilitate the DFSS composting process and, as a consequence, a higher dosage of biochar could be a sustainable way of managing agricultural waste. Adding wheat-straw biochar to DFSS was considerably increased the water-soluble (AP, DOC, DON, and NO_3^--N) and total nutrients (TKN, TP, TK and TNa), led to faster degradation of organic matter and reduced the maturity period by 3 weeks with accelerated stabilization and detoxification. The optimal dosage of biochar combined with zeolite were 12%+15% (dry weight basis) under the conditions of the present study, in which composting was carried out for 56 days. Furthermore, the application of biochar amended compost into soil was more effective in increasing the available essential nutrients concentration and improving the soil fertility. Nevertheless, depending on the compost dosage, the biomass of Chinese cabbage was considerably increased after 150 kg ha^{-1} compost treatments, whereas the maximum yield was obtained at 150 kg ha^{-1} 12%B+15%Z amended compost. Thus, biochar combined with zeolite for DFSS composting is beneficial for reducing the maturity period, and enriching biochar with zeolite compost in the soil can increase the water-soluble macro-nutrients and thereby enhance the benefits of its application for organic farming derived from the added nutrients.

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