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Performance evaluation of gaseous emissions and Zn speciation during Zn-rich antibiotic manufacturing wastes and pig manure composting

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A B S T R A C T

In this study, the co-composting performance of Zn-rich antibiotic manufacturing wastes (AMW) and pig manure (PM) was evaluated. Four treatments, representing 2.5%, 5%, 10% and 20% of AMW (of PM dry weight) and control without AMW, were established during composting. Results suggested that the temperature, pH, electrical conductivity, NH_4^+-N and germination index in end product met the maturity and sanitation requirement. More than 99% of residual antibiotic was removed. Compared with PM composting alone, the cumulative CH_4 and N_2O emissions in AMW composting increased by 13.46–79.00% and 10.78–65.12%, respectively. While the higher mixing ratios of AMW (10% and 20%) presented a negative impact on composing by inhibiting organic matter (OM) degradation and higher NH_3 emissions. The AMW had highly bioavailable Zn, but the exchangeable faction of Zn significantly decreased with the composting progress.

1. Introduction

Nowadays, China has become one of the largest antibiotic producers and exporters in all over the world, which accounts for 20–30% of the world's production of antibiotic manufacturing wastes (AMW) in the early 2008 (Wu et al., 2011). AMW are kinds of industrial fermentation bio-wastes which contain considerable quantity of nutritional substances (i.e., starch, maize slurry, protein and amino acids) (Xiao et al., 2015; Yang et al., 2016), and also included high levels of residual antibiotics and heavy metals (zinc and copper, etc) (Ding et al., 2014; Zhang et al., 2018a). This AMW were once transported to the environment without proper disposing, might increase the risk of generation and spread of antibiotic resistance genes in food chain (Zhang et al., 2015). Therefore, AMW were classified as one of the hazardous solid wastes by the Chinese government (The People's Republic of China Ministry of Environmental Protection and National Development and Reform Commission, 2008). Additionally, the huge quantity of PM generation (~490 million tons in 2015) was also attracted more and more attention to Chinese government due to their high nutritional value and resource loss (NBSC, 2016; Li et al., 2012). But its direct application caused some serious environmental issue such as soil and water pollutions and the obnoxious odor emission (Jensen et al., 2018; Orzi et al., 2018; Wang et al., 2018). Hence, it is necessary to introduce a practical and economical feasible technology for degradable organic waste management (Li et al., 2018).

For the aim of nutrients recycling, composting is a biological process that reduce the environmental risk of AMW and PM as well as promotes the conversion of stable and hygienic end product for land utilization (Zhang et al., 2015; Zhang et al., 2018a; Yang et al., 2016). Residue antibiotics such as β-lactam, aminoglycosides, tetracycline, sulfonamide and macrolide in AMW and other organic solid wastes could be effectively removed during composting (Liu et al., 2017; Selvam et al., 2012; Yang et al., 2016; Zhang et al., 2018a). Zhang et al. (2015) reported that about 99.95% of penicillin was decreased within first 10 days in penicillin fermentation fungi residue and PM co-composting. Similarly, Ho et al. (2013) identified that the removal rate of erythromycin during broiler manure composting was approximately 100%. Composting is regarded as a feasible approach to recycling organic waste, but gaseous emissions during the composting were also adversely affected to the surrounding environment (Awasthi et al., 2016; Wang et al., 2013a,b). CH_4 and N_2O have 25 and 296 times higher global warming potential than CO_2, which are highly responsible for the atmospheric pollution (IPCC, 2015).

Additionally, ammonia volatilization during composting process not only causes the nitrogen loss, but also has the potential risk of global warming (Awasthi et al., 2018; Santos et al., 2017; Wang et al., 2016b). Thus, gaseous emissions are one of the major challenges that cannot be ignored during composting (Awasthi et al., 2016, 2018; Santos et al.,

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2017; Zhang et al., 2017a,b). Santos et al. (2017) demonstrated that the proper mixing ratio of spent coffee grounds with *Acacia dealbata* shoots and wheat straw was 40%, which could have a lower greenhouse gases emissions during composting. Sawdust as a bulking agent could also release less greenhouse gases than cornstalks and spent mushroom substrate during kitchen waste composting (Yang et al., 2013). Meanwhile, some additives, such as biochar (Awasthi et al., 2017a,b; Wang et al., 2018), medical stone (Awasthi et al., 2018) and struvite (Jiang et al., 2016) amendments were founded to be effective to mitigate the gaseous emissions. However, the gaseous emissions during different kinds of organic wastes composting are widely reported, but composting of PM combined with AMW has not been previously identified.

Simultaneously, the use of flocculants during antibiotics production process, such as $ZnSO_4$, lead to the high content of Zn in AMW (Ding et al., 2014; Xiao et al., 2015), which did not receive proper consideration in AMW management. Because heavy metals could exist for prolonged time in the environment, and its high concentration might inhibit the metabolic microbial activities of composting (Zhang et al., 2018a). Recycling AMW was also urgent to harmless treatment of its Zn at the same time. The literatures reported that the addition of Zn in anaerobic digestion increased the biogas production (Zhang et al., 2017b), and the bioavailability of heavy metals could reduce during aerobic composting (Wang et al., 2016a,b). To the best of our knowledge, very limited studies were investigated the feasibility of Zn-rich AMW composting and their effects on composting performance as well as its correlation of gaseous emission with physicochemical parameters.

Therefore, the main objectives of this investigation were: (1) to evaluate the feasibility of co-composting of Zn-rich AMW with PM at different rates; (2) to identify the gaseous emissions (CH_4, N_2O and NH_3) and the degradation of antibiotic during composting and; (3) to examine the variations of bioavailable Zn based on its speciation. Hence, the results from this research can provide some baseline about the centralized management and harmless disposal of Zn-rich AMW as well as the performance of Zn-rich AMW and PM co-composting.

2. Materials and methods

2.1. Source of materials

AMW used in this study were typical by-product during the erythromycin production process with high concentration of Zn (141240 ± 1323 mg kg^{-1}), which were obtained from a local pharmaceutical company, Shaanxi, China. Due to the high moisture content of fresh AMW (78.58 ± 2.42%) and the single microbial community species. The preliminary experiment showed that Zn-rich AMW composting alone cannot achieve the thermophile phase (temperature was below 50 °C throughout the composting process). In this study, PM was used as another common composting material to accelerate the composting and dilute contaminants. The PM (produced by pig fed with food residues with no additives) and wheat straw (WS) were collected from a rural pig farm and a local farmland, Yangling town, Shaanxi, China. WS was crushed to 1 cm fragments after air dry, and then used as bulking agent to adjust the C/N ratio, moisture content and bulking density. The main physicochemical characteristics of composting feedstock's are listed in Table 1.

2.2. Composting experiments and sampling

The compost reactors made of Polyvinyl chloride plate with the working volume of 100 L were used in this study. The airflow rate was according to the previous operating procedures reported by Li et al. (2012). Considering the Zn concentration of PM in China, from 39.5 to 11378.9 mg kg^{-1} (Wang et al., 2013b), the experimental design was based on the reports by Zhang et al. (2018a), who studied their research works according to the metals residue level of sewage sludge. The PM and WS were mixed thoroughly at the ratio of 3:2 (on dry weight basis).

Table 1
Physicochemical properties of the raw materials in this experiment.

Parameter	AMW[a]	PM[a]	WS[a]
Moisture content (%)	78.58 ± 2.42	71.12 ± 0.35	5.15 ± 0.77
pH	7.45 ± 0.03	7.63 ± 0.12	6.60 ± 0.20
Electrical conductivity (mS cm^{-1})	3.64 ± 0.05	5.23 ± 0.19	1.80 ± 0.61
Organic matter[b] (%)	69.35 ± 0.12	78.19 ± 0.08	90.91 ± 0.89
Total Kjeldahl nitrogen[b] (g kg^{-1})	33.16 ± 1.09	26.02 ± 0.11	5.93 ± 0.61
Carbon/nitrogen ratio	12.15 ± 0.51	17.43 ± 0.08	89.55 ± 9.24
Ammonium nitrogen (g kg^{-1})	2.82 ± 0.06	2.20 ± 0.11	0.37 ± 0.21
Nitrate nitrogen (mg kg^{-1})	32.56 ± 4.23	23.07 ± 0.43	11.74 ± 0.94
Zn[b] (mg kg^{-1})	141240 ± 1323	137.4 ± 4.54	73.91 ± 2.85
Cu[b] (mg kg^{-1})	16.52 ± 0.74	72.12 ± 1.25	7.42 ± 0.73

[a] AMW = antibiotic manufacturing wastes; PM = pig manure; and WS = wheat straw.
[b] Dry weight basis.

Table 2
Experimental design in this experiment.

Treatment	AMW (%)[a]	Initial C/N ratio[b]	Initial Zn (mg kg^{-1})[c]
T1/Control	0	27.42	123.8
T2	2.5	27.25	2268
T3	5	25.66	4263
T4	10	24.73	8083
T5	20	23.21	15,109

[a] The percentage of antibiotic manufacturing wastes (AMW) was based on the dry weight of pig manure (PM).
[b] The initial total carbon to total nitrogen ratio of feed stock.
[c] Dry weight basis.

Five different mixing ratios of AMW and PM were designed, namely T1-T5 to evaluate the performance of gaseous emissions and Zn speciation (Table 2). The compost and environmental temperatures were monitored two times each day and the average temperatures recorded. Samples were randomly collected from every composting vessel after properly mixed on 0, 3, 7, 14, 21, 35, 42 and 50 d. Each sample was subdivided and then stored in two different environments: one was preserved at 4 °C as fresh sample, and the rest of sample was dried for physicochemical analyses.

2.3. Physicochemical properties and gas analyses

The pH, electrical conductivity (EC), ammonium nitrogen (NH_4^+-N) and nitrate nitrogen (NO_3^--N) were measurement according to TMECC (2002). The pH and EC of each samples were determined in aqueous extracts (1:5 w/v) by MP521 pH/EC meter (Shanghai, China). NH_4^+-N and NO_3^--N were monitored by the Segmented Flow Analyzer (Technicon Auto-analyzer II System, Germany) using the 2 mol/L KCl extracts at 1:10 (w/v) ratio for 0.5 h. Germination index (GI) was detected according to the method previously reported by Zucconi et al. (1981). The air-dried compost samples were ignited at 550 °C in a muffle furnace for 24 h to detect the content of OM. Gas samples were taken daily in the first 2 weeks and then once in two days, while the concentration of CH_4 and N_2O were detected by gas chromatography (Agilent Technologies 6890 N Network GC system, China) and NH_3 was adsorbed in 2% boric acid and titrated with 1 mol/L hydrochloric acid as mentioned by Awasthi et al. (2016). The residual erythromycin during composting was extracted and analyzed according to the method described by Ho et al. (2013) and Topp et al. (2016).

2.4. Sequential extraction

Factions of Zn were measured according to the modified BCR