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Effect of different struvite crystallization methods on gaseous emission and the comprehensive comparison during the composting

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HIGHLIGHTS

- Struvite crystal formation reduces NH_3 loss by 51–82%.
- SO_4^{2-} reduces CH_4 emission by 62–70%.
- $Mg(OH)_2 + H_3PO_4$ treatment yields the highest struvite content in the end product.
- $MgSO_4 + H_3PO_4$ treatment yields the lowest struvite content due to low pH.
- $Ca(H_2PO_4)_2 + MgSO_4$ treatment is most suitable for practical use.

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ABSTRACT

This study compared 4 different struvite crystallization process (SCP) during the composting of pig feces. Four combinations of magnesium and phosphate salts ($H_3PO_4 + MgO$ (PMO), $KH_2PO_4 + MgSO_4$ (KPM), $Ca(H_2PO_4)_2 + MgSO_4$ (CaPM), $H_3PO_4 + MgSO_4$ (PMS)) were assessed and were also compared to a control group (CK) without additives. The magnesium and phosphate salts were all supplemented at a level equivalent to 15% of the initial nitrogen content on a molar basis. The SCP significantly reduced NH_3 emission by 50.7–81.8%, but not the N_2O. Although PMS group had the lowest NH_3 emission rate, the PMO treatment had the highest struvite content in the end product. The addition of sulphate decreased CH_4 emission by 60.8–74.6%. The CaPM treatment significantly decreased NH_3 (59.2%) and CH_4 (64.9%) emission and yielded compost that was completely matured. Due to its effective performance and low cost, the CaPM was suggested to be used in practice.

1. Introduction

Composting is a widely-used and effective technology for the utilization of organic waste. However, the process emits harmful gasses, such as ammonia (NH_3), as secondary pollution. During composting of animal waste about 9.6–46% of the initial nitrogen is lost in the form of NH_3, which accounts for 79–94% of the total nitrogen loss (Jiang et al., 2011; Fukumoto et al., 2011; Yang et al., 2015). NH_3 emission causes not only a decline of compost quality, but also serious environmental problems such as odor and haze (Jiang et al., 2015). In northern China, ammonium has been shown to be a significant and increasing component of airborne fine particles (PM2.5): from 2003 to 2012, its proportion has increased from 7.5% to 12% (Li et al., 2013).

Several approaches have been taken to reduce the volatilization of NH_3 during composting, including optimization of the composition of raw materials, use of different bulking agents (Nakhshiniev et al., 2014; Chowdhury et al., 2014), improvement of composting process conditions (El Kader et al., 2007), use of chemical additives (Liu et al., 2015; Yang et al., 2015), and use of microbial amendments (DeLaune et al., 2004). Struvite crystallization process (SCP) which was first used in the treatment of waste water, has recently been used in composting (Jeong and Kim, 2001; Lee et al., 2009; Wang et al., 2013).The SCP can decrease NH_3 emission by generate struvite ($MgNH_4PO_4 \cdot 6H_2O$), a high-quality, slow-release fertilizer.

In previous work, different magnesium (Mg) salts (e.g., $Mg(OH)_2$, $MgCl_2$, $MgSO_4$) and phosphorus (P) salts (e.g., H3PO4, KH_2PO_4, NaH2PO4, Na_2HPO_4) were used for struvite formation, but no published study has specifically evaluated the effect of different Mg and P salts on struvite crystal formation and gaseous emission.

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The purpose of the present study was to identify the most valuable and practical SCP method for composting by evaluating the differences of 4 struvite precipitation methods on N conservation, greenhouse gas emission, struvite crystal formation, and the cost balance.

2. Methods

2.1. Raw materials and composting installation

Pig feces and cornstalk were mixed at a ratio of 7:1 (w/w) as raw materials. Pig feces were taken from a pig fattening farm located in Beijing. Air-dried corn stalk was obtained from the Shangzhuang research station of China Agricultural University. The compositions of the raw materials and the mixture are shown in Table 1. Although the *C*/*N* ratio is lower than the traditionally suggested level, it is similar to ratios seen in current practice in Chinese compost plants.

Experiment was carried out in a laboratory-scale composting system (Fig. 1). Each compost vessel in this system had a capacity of 60 L and was controlled by a composting program. Under this program, the aeration was controlled automatically. The temperatures in the vessels were also recorded by the program at 02:00 and 14:00 every day.

2.2. Experimental design and sample collection

Five treatments were conducted in triplicate to evaluate the effects of the different MAP methods (Table 2). According to the results of previous researches (Jeong and Hwang, 2005; Ren et al., 2010), the P and Mg salts were all supplemented at a level equivalent to 15% of the initial nitrogen content on a molar basis. All the P and Mg salts were gotten form agriculture market as chemical fertilizer, not the analytical reagents. In the CaPM treatment, triple superphosphate (with P_2O_5 content of 46%) was used instead of pure $Ca(H_2PO_4)_2$. Continuous aeration at a rate of 0.3 L kg^{-1} DM min^{-1} was employed in all treatments. The materials were composted for 5 weeks and turned at days 4, 10, 18, and 26 in order to homogenize the materials and improve porosity.

Samples of approximately 100 g were taken for analysis at the beginning of the experiment, during each turning, and at the end of the experiment. Samples were divided into two parts: one part was air-dried and ground to pass through a 0.1 mm sieve as a dry sample; the other part was immediately frozen as a fresh sample.

2.3. Analytical methods and calculations

Total nitrogen (TN) and total organic carbon (TOC) content were measured by an elemental analyzer (Elementar vario MACRO cube, Germany). Mineral compositions were analyzed by a powder X-ray diffraction analyzer (Rigaku Dmax 12 kW, Japan). Fresh samples were mixed with deionized water at a ratio of 10:1 (w/w) and shaken for 30 min, and then filtered. The supernatant was then collected for measurement of germination index (GI) (Guo et al., 2012). NH_4^+ and NO_3^- were extracted with 2 M KCl (1:20) and were analyzed by a segmented flow analyzer (Technicon Autoanalyzer II system, Germany).

CH_4 and N_2O content were analyzed by gas chromatographs (Agilent 7890A, USA) equipped with electron capture and flame ionization detectors, respectively (Jiang et al., 2011). The O_2 were analyzed by gas chromatograph equipped with thermal conductivity detector (Beifen 3420A, China). The NH_3 was absorbed by a washing bottle with boric acid (2%) and then titrated using 0.05 M H_2SO_4. Gas emission rates (N_2O, CH_4, NH_3) were measured daily during the first 2 weeks, and then 3–4 times per week thereafter. Based on previous experience, N_2O increases rapidly after turning the compost. Thus, after each turning, the N_2O was measured hourly until the emission rate declined to a constant level. Cumulative emissions for the whole composting period were calculated from the daily flux. Data for non-measured days were obtained by averaging that of the closest measured days.

All data were analyzed using One-way Analysis of Variance (ANOVA). LSD-t was used to test for significant differences. SPSS 17 for Windows was used for all statistical analyses.

3. Results and discussion

3.1. Evolution of temperature and oxygen concentration

Once the experiment began, the temperature of all treatments increased quickly (Fig. 2A). For all except the PMS group, the temperature exceeded 65 °C after 3 days. The duration of the thermophilic phase of these treatments was approximately 2 weeks, which is a sufficient length of time to achieve a sanitation effect. With the exhaustion of easily degradable carbon, the temperatures decreased gradually and approached air temperature after 4 weeks. The temperature of the PMS treatment group was significantly lower than that of CK ($P = 0.033$), and its thermophilic phase lasted only five days. The addition of $H_3PO_4 + MgSO_4$ (PMS treatment) inhibited the degradation process significantly. Lee et al. (2009) reported that both Mg ($MgCl_2$) and P (KH_2PO_4) salts inhibit organic matter decomposition during composting when present in molar ratios of greater than 0.05 with regard to TN. In this study, significant inhibition was not observed in the CaPM ($Ca(H_2PO_4)_2 + MgSO_4$) or KPM ($KH_2PO_4 + MgSO_4$) treatment, even when the salts were added at a concentration of 15% (mole/mole) of the initial nitrogen content. Jeong and Hwang (2005) reported that the optimal dose of Mg and P salts should be approximately 20% (mole/mole) of the initial nitrogen content to ensure both the complete mineralization of organic materials and increased conservation of nitrogen. In our research, the addition of $H_3PO_4 + MgSO_4$ significantly decreased the pH value (Fig. 3), which is likely responsible for the low degradation rate. The low pH not only inhibits the composting process directly, but also increases the accumulation of VFAs and NH_4^+ in the compost that further enhances the inhibition on degradation of organic matter (Wong et al., 2009; Wang et al., 2013).

Due to intensive degradation, the O_2 content in the outlet for all treatments decreased to 8–13% by the second day and maintained this low level for approximately 1 week (Fig. 2B). After that, the O_2 content began to increase until it gradually reached the air

Table 1
Compositions of raw materials and mixture.

	TOC (g kg^{-1} DM)	TN (g kg^{-1} DM)	NH_4^+-N (g kg^{-1} DM)	NO_3^--N (mg kg^{-1} DM)	MC (%)	*C*/*N*
Pig feces	349 ± 22.1	26.5 ± 2.1	6.1 ± 1.2	116.2 ± 15.1	77.8 ± 2.1	13.2 ± 0.8
Corn stalk	419 ± 8.2	9.9 ± 0.7	–	–	9.3 ± 0.2	42.3 ± 0.7
Mixture	374.8 ± 11.8	20.4 ± 2.9	3.8 ± 0.9	73.8 ± 10.2	69.2 ± 3.8	18.4 ± 0.5

DM, dry matter; TOC, total organic carbon; TN, total nitrogen; MC, moisture content; – , undetected.