

Effect of different amendments on nitrogen conservation during simulated composting

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Abstract: **[Purpose]** The objectives of this study were to evaluate the effects of different dosages of three amendments—peat, superphosphate, mixture of magnesium hydroxide and phosphorus acid [$\text{Mg}(\text{OH})_2+\text{H}_3\text{PO}_4$] on nitrogen conservation. **[Methods]** The simulated composting experiment was carried out in a constant temperature water bath with pig manure and corn straw. **[Results]** The results showed that the ammonia volatilization could be inhibited to some extent under the treatments with fixing agents. Under the same simulated composting conditions, the nitrogen fixation effect of the three kinds of fixatives with the same proportion was as follows: $\text{Mg}(\text{OH})_2+\text{H}_3\text{PO}_4$ >superphosphate>peat. The fixation effect of nitrogen increased with the increase of the additives. The nitrogen fixation rate of $\text{Mg}(\text{OH})_2+\text{H}_3\text{PO}_4$ treatment was up to 66%. Compared with the control group, the amount of cumulative ammonia emission decreased by 90.3% and the total nitrogen content increased by 39.31% in this treatment. Compared with other two kinds of fixing agents, $\text{Mg}(\text{OH})_2+\text{H}_3\text{PO}_4$ treatment could not only control nitrogen loss in composting process, improve the nitrogen nutrient content of compost products, but also could increase phosphorus and magnesium nutrients. **[Conclusions]** Therefore, it had more popularization value and application prospect.

Keywords: simulated composting, amendment, effect of nitrogen conservation.

1. Introduction

Composting is one of the most important methods to realize the recycling and utilization of waste resources such as straw and livestock manure [1]. However, the nitrogen loss in the composting process could not only reduce the nutrient content and fertilizer efficiency of fertilizer, but also aggravate the environmental pollution [2] and become an important source of fine particulate matter (for example, PM_{2.5}) in the air [3]. At present, there are two main methods to control nitrogen loss: the one is to change the process conditions, such as appropriate C/N, pH, temperature, moisture content, ventilation, turnover frequency, etc [4]. The other is to use additives in the composting process. The common are physical, chemical and biological amendments, such as zeolite, biochar, metal salts, phosphates, nitrogen-fixing bacteria, EM bacteria, etc. In previous work, different magnesium (Mg) and phosphorus (P) salts were used as nitrogen fixing additives for struvite crystallization process. This process could decrease ammonia emission by generate struvite crystal ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), which was a poor water soluble, high-quality, slow-release fertilizer [5-7]. Several scholars have studied the effect of a certain type of additive on nitrogen morphological transformation in the composting process [8-9], but lack of comprehensive comparative evaluation and analysis of several additives.

Based on the rule of nitrogen loss in composting process, the objectives of this study were to evaluate the effects of three amendments [peat, superphosphate, $\text{Mg}(\text{OH})_2+\text{H}_3\text{PO}_4$] at different dosages on nitrogen conservation during simulated composting. The best kind and amount of nitrogen fixation material were selected to provide a reliable nitrogen loss control scheme for the development of composting.

2. Material and methods

2.1 Raw materials

In this experiment, fresh pig manure and corn straw were used as compost materials. The pig manure was taken from the sujiatuo pig farm in haidian district, Beijing. The cornstraw was taken from the

experimental field in the science park of China agricultural university, which was cut into about 1 cm fragments. The basic properties of raw materials were shown in table 1. Peat, superphosphate, $\text{Mg}(\text{OH})_2+\text{H}_3\text{PO}_4$ were chemically pure, which were added to the materials for composting.

Table 1

The properties of raw materials

	pig manure	cornstalk
TOC ($\text{g}\cdot\text{kg}^{-1}$ DM)	370±3.18	430±3.32
TN ($\text{g}\cdot\text{kg}^{-1}$ DM)	19.3±0.62	11.1±0.04
$\text{NH}_4^+\text{-N}$ ($\text{g}\cdot\text{kg}^{-1}$ DM)	0.97±0.01	--
EC ($\text{ms}\cdot\text{cm}^{-1}$)	3.78±0.14	2.15±0.09
C/N	19±0.49	39±0.36
pH	8.5±0.22	7.7±0.34
MC (%)	72±0.63	23±0.21

DM, dry matter; TOC, total organic carbon; TN, total nitrogen; $\text{NH}_4^+\text{-N}$, ammonium nitrogen; EC, electrical conductivity; MC, moisture content; --, undetected.

2.2 Experimental design and sample collection

Urea (pure carbon and nitrogen source) was used to adjust C/N of the raw materials to 20. The nitrogen fixatives—peat, superphosphate, and $\text{Mg}(\text{OH})_2+\text{H}_3\text{PO}_4$ were named A, B, and C and were also compared to a control group (CK) without additives. Three replicates were set for each treatment and the experimental design was shown in table 2. Urea dissolved in the aqueous solution completely, and then spread and mixed in raw materials evenly. The moisture content of the materials was controlled to 70%. Composting sealed fermentation bottles with capacity of 1 L were placed in a thermostatic water bath with adjustable temperature, and the temperature control simulated the outdoor composting temperature. Forced mechanical intermittent ventilation was adopted, and the ventilation rate was controlled at about $0.1 \text{ m}^3/(\text{min}\cdot\text{m}^3)$ for half an hour with a one-hour interval. The test lasted for 10 days and the test apparatus was shown in figure 1.

Table 2

The dry weight proportion of composting materials and the dosage of adsorbents

Treatments	Pig Manure (%)	Cornstalk (%)	Urea (%)	Additive (%)	MC (%)	C/N	Type of Additive
CK	16.67	12.90	0.43	0 ^a	70	20	--
A1	53.43	41.35	1.38	3.85	70	20	Peat
A2	52.42	40.57	1.35	5.66	70	20	
A3	51.45	39.81	1.33	7.41	70	20	
A4	50.51	39.09	1.30	9.09	70	20	
B1	53.43	41.35	1.38	3.85	70	20	Superphosphate
B2	52.42	40.57	1.35	5.66	70	20	
B3	51.45	39.81	1.33	7.41	70	20	
B4	50.51	39.09	1.30	9.09	70	20	
C1	53.43	41.35	1.38	3.85 (1:1) ^b	70	20	$\text{Mg}(\text{OH})_2+\text{H}_3\text{PO}_4$
C2	51.45	39.81	1.33	7.41 (1:2)	70	20	
C3	50.51	39.09	1.30	9.09 (1:3)	70	20	

^a Dry weight ratio; ^b Molar ratio of $\text{Mg}(\text{OH})_2$ to H_3PO_4

During the experiment, Samples of approximately 100 g were taken at 0, 3, 6, 8 and 10 days,

respectively. Accurate weighing was performed before and after each sampling to calculate the material balance. The sample was divided into two parts: one part was fresh sample, which was used to measure water content and other water-soluble indexes; the other part was air-dried and ground to pass through a 0.1 mm sieve as a dry sample. The moisture content in the compost was calculated according to the moisture content in the sample, which was used as the basis for supplementing the moisture content and keeping it 70%. The nitrogen fixation rate was calculated and the nitrogen control effect of the fixatives in composting process was studied.

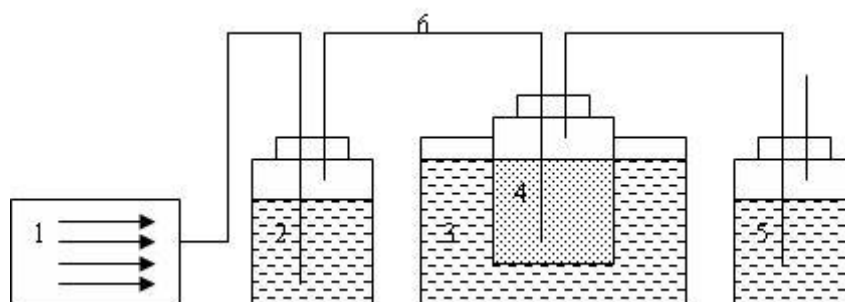


Fig 1 Structure of simulated composting equipment 1. pump; 2. filter humidifier; 3. constant temperature water bath; 4. compost materials; 5. 2% boric acid; 6. catheter

2.3 Analytical methods and calculations

The moisture content of the samples was determined by drying at 105 °C for 8 h. TN content were measured by an elemental analyzer (Elementar vario MACRO cube, Germany). $\text{NH}_4^+\text{-N}$ was extracted with 2 M KCl (1:20) and was analyzed by a segmented flow analyzer (Technicon Autoanalyzer II system, Germany). The NH_3 was absorbed by a washing bottle with boric acid (2%) and then titrated using 0.1 M H_2SO_4 . Calculation method of nitrogen loss rate and fixation rate:

$$\text{Nitrogen loss rate } X = (M_0 \times N_0 - M_1 \times N_1) / (M_0 \times N_0) \times 100\% \quad (1)$$

$$\text{Nitrogen fixation rate } Y = (X_{\text{CK}} - X_{\text{Treatment}}) / X_{\text{CK}} \times 100\% \quad (2)$$

Where M_0 is the initial weight of materials, dry weight, g; M_1 is the weight of the sample material on day 10, dry weight, g; N_0 is the total nitrogen content in the initial material, %; N_1 is the total nitrogen content of the sample material on day 10, %.

All data were analyzed using One-way Analysis of Variance (ANOVA). SPSS 17 for Windows was used for all statistical analysis.

3. Results and discussion

3.1 Temperature

The test temperature was simulated to the composting temperature outdoor. Constant temperature water bath control was adopted in three stages of heating, high temperature and cooling. The high temperature phase lasted for five days (50°C or higher) and the temperature change was shown in figure 2.

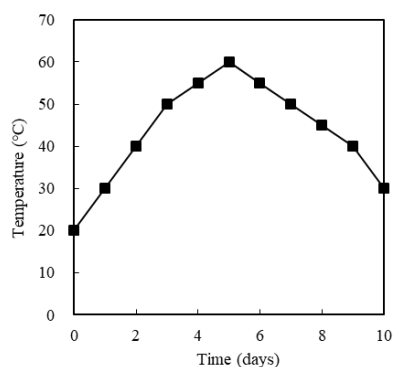


Fig 2 The temperature changes during composting

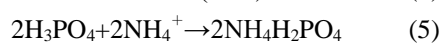
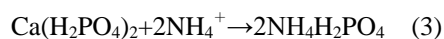
3.2 Nitrogen changes during simulated composting

3.2.1 Ammonia emission

As could be seen from figure 3, only a small amount of ammonia gas was released during the 0-3 days of the heating period, and the ammonia emission amount accounted for 3.11%~14.91% of the total emission amount (table 3). The high temperature period was the peak period of ammonia release, and the ammonia release amount was significantly increased in 3-6 days. The cumulative ammonia emission amount accounted for 39.42%~69.24% of the total amount. During 6-8 days, with the gradual decrease of composting temperature, the ammonia amount decreased, and the cumulative ammonia amount accounted for 13.19%~51.58% of the total release amount. After 8 days, ammonia release decreased and stabilized, accounting for only 1.22%~6.89% of the total amount. Ammonia emissions decreased gradually with the increase of the amount of fixative (fig.3), indicating that the greater the proportion of fixative within the range of the experimental design, the better the fixation effect on ammonia nitrogen.

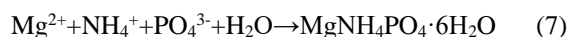
Compared with the control group, the three fixatives all controlled the ammonia volatilization to different extent. Under the same addition ratio, the $Mg(OH)_2+H_3PO_4$ treatment had the highest reduction rate, which was 90.28% compared with the control. The treatment of superphosphate was the next (76.13%), the last one was the peat treatment (53.44%).

The effect of ammonia emission reduction was different due to the different fixation principles of nitrogen fixing agents. Peat was the remains of marsh plants, with organic matter content of more than 30%. The pH ranged from 5.0 to 6.9, showing slightly acidic, which could absorb and fix ammonia emission to some extent. At the same time, its own nutrients could improve the fertility of compost products [10-11]. The main components of superphosphate were monocalcium phosphate monohydrate $[Ca(H_2PO_4)_2 \cdot H_2O]$, containing 14%~20% of available phosphorus (P_2O_5), 40%~50% of calcium sulfate, and 3.5%~5% of free sulfuric acid and phosphoric acid. Studies have shown that the pH value of its saturated solution was 1.48, which was acidic. By adding superphosphate, ammonia volatilization could be reduced by reducing the pH value of compost materials, and the following reactions may occur to generate relatively stable acidic ammonium phosphate or ammonium sulfate, so as to fix NH_4^+ -N and reduce the loss of nitrogen [12].



Different proportions of $Mg(OH)_2$ and H_3PO_4 were mixed to produce an emulsion that was not completely soluble in water. It was a mixture containing $MgHPO_4$, $Mg(H_2PO_4)$, $Mg_3(PO_4)_2$ and their

crystalline water, which could react with ammonia:



Struvite crystal ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) was also a kind of high-quality inorganic fertilizer, which not only had a good fixation effect on ammonia, but also increased the content of phosphorus in the compost. Therefore, it was an ideal compost additive [13].

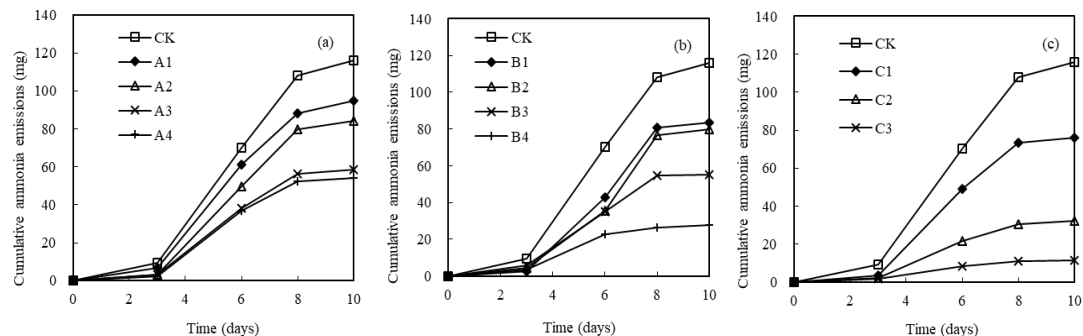


Fig 3 Cumulative ammonia emissions of different treatments (a) peat, (b) superphosphate, (c) $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$. CK, control; A1, 3.85% peat; A2, 5.66% peat; A3, 7.41% peat; A4, 9.09% peat; B1, 3.85% superphosphate; B2, 5.66% superphosphate; B3, 7.41% superphosphate; B4, 9.09% superphosphate; C1, 3.85 $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$; C2, 7.41% $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$; C3, 9.09% $\text{Mg}(\text{OH})_2 + \text{H}_3\text{PO}_4$

Table 3

The proportion of ammonia emission amount in each phase to the total emission amount

Treatments	Proportion (%)			
	0~3 d	3~6 d	6~8 d	8~10 d
CK	8.10	52.29	32.72	6.89
A1	7.32	57.30	28.64	6.74
A2	3.98	55.05	35.87	5.09
A3	5.81	58.85	30.98	4.36
A4	3.88	64.21	28.40	5.19
B1	3.11	48.19	45.32	3.38
B2	5.27	39.42	51.58	3.73
B3	10.17	53.07	35.53	1.22
B4	12.09	69.24	13.19	5.48
C1	4.38	60.40	31.54	3.67
C2	6.60	60.12	27.53	5.74
C3	14.91	58.79	24.67	1.62

3.2.2 TN

The change of total nitrogen content in simulated composting with different treatments was shown in figure 4, and the total nitrogen content in the treatments with additives was significantly higher than that in the control group. More the fixative added, higher the total nitrogen content was. In the first 3 days of composting, all treatments with a ratio of 3.85% showed a downward trend, which may be due to the conversion of part of ammonium nitrogen into ammonia volatilization, and only a small amount of degradation of the material itself. In the treatment of 5.66% and 7.41%, only the total nitrogen content of the peat decreased slightly in the first 3 days. The total nitrogen content of the compost material increased gradually with the addition ratio of 9.09%, indicating that the additive had a fixation effect on

the nitrogen of the compost material. With the progress of composting, organic matter began to degrade violently. Because of the double effects of concentration and fixation, the total nitrogen content of amendment treatments presented an increasing trend. The peak period of ammonia generation was 4~6 days, and the rising period of total nitrogen content was less than 6~8 days generally.

At the end of the experiment, compared with the control group, the total nitrogen content of the fixative with the addition of 3.85% increased by 2.53%, 9.08% and 13.08%, respectively. The addition amount of 5.66% increased by 9.40% and 18.77%. The addition amount of 7.41% increased by 10.85%、18.19% and 32.76%, respectively. The total nitrogen content of 9.09% addition amount increased by 20.28%, 31.11% and 39.31%, respectively.

Compared with different fixatives, it could be seen that no matter which amount of addition, the treatment of $Mg(OH)_2+H_3PO_4$ had the highest total nitrogen content, followed by the treatment of superphosphate and peat. The results showed that $Mg(OH)_2+H_3PO_4$ treatment had the best nitrogen fixation effect among the three fixatives. There was no significant difference between the treatment with a proportion of 3.85% additives and the control (P values were 0.475, 0.212 and 0.132, respectively), while the difference between the other treatments and the control was significant, indicating that the nitrogen fixation effect on compost was limited when the dosage was low. The difference of the same additive in different proportion was extremely significant. The variance analysis between treatments with different proportions of peat was $F=5.9$, $P=0.003^*$, variance analysis between superphosphate treatments was $F=4.8$, $P=0.007^*$, and $Mg(OH)_2+H_3PO_4$ treatment was $F=6.0$, $P=0.006^*$.

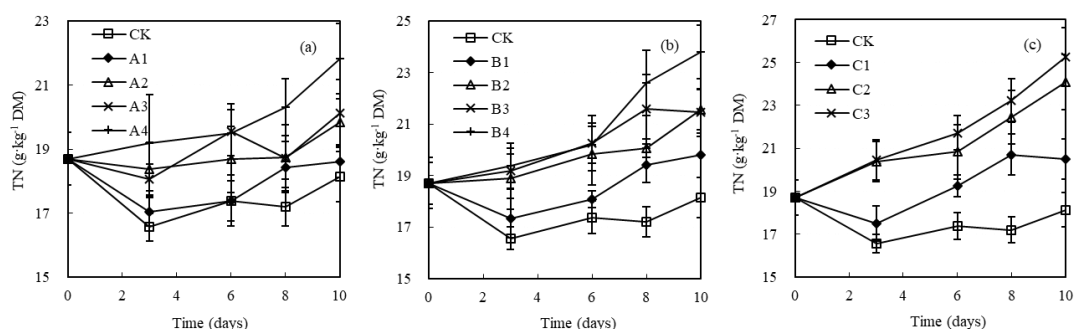


Fig 4 Total nitrogen content of different treatments (a) peat, (b) superphosphate, (c) $Mg(OH)_2+H_3PO_4$. CK, control; A1, 3.85% peat; A2, 5.66% peat; A3, 7.41% peat; A4, 9.09% peat; B1, 3.85% superphosphate; B2, 5.66% superphosphate; B3, 7.41% superphosphate; B4, 9.09% superphosphate; C1, 3.85 $Mg(OH)_2+H_3PO_4$; C2, 7.41% $Mg(OH)_2+H_3PO_4$; C3, 9.09% $Mg(OH)_2+H_3PO_4$

3.2.3 NH_4^+-N

The variation trend of NH_4^+-N with three fixatives was shown in figure 5. In the CK group, NH_4^+-N showed a declining trend, from $2.78\text{ g}\cdot\text{kg}^{-1}\text{ DM}$ at the beginning to $1.75\text{ g}\cdot\text{kg}^{-1}\text{ DM}$, which was due to the large amount of NH_4^+-N converted into NH_3 in the high temperature period. However, the ammonium nitrogen was fixed in the treatments with fixatives by different principles, which showed an upward trend.

Except for the low proportion treatment of A1, due to the large ammonia volatilization in the early stage of the peat treatment, the ammonia first dropped and then rose. In addition, the other treatments showed a gradually increasing trend, and with the increase of the addition proportion, the content of NH_4^+-N also gradually increased. At the end of the experiment, four adding proportion ammonium nitrogen content were 3.26 , 4.37 , 5.57 and $6.89\text{ g}\cdot\text{kg}^{-1}\text{ DM}$, was 1.8~3.9 times of the control, one-way analysis of variance results showed that the difference among treatments was extremely significant ($F = 6.7$, $P = 0.001$). NH_4^+-N was fixed by reducing the pH value of materials and chemical reaction, and the

fixation effect was better than peat. At the end of the experiment, the contents of $\text{NH}_4^+\text{-N}$ in the four added proportions were 5.09, 5.55, 6.81 and 8.13 $\text{g}\cdot\text{kg}^{-1}$ DM, respectively, which was 2.9~4.6 times higher than that of the control treatment, and the difference between treatments was significant ($F=3.54$, $P=0.024$).

Compared with the other two fixatives of the same proportion, $\text{Mg}(\text{OH})_2+\text{H}_3\text{PO}_4$ treatment had the higher ammonium nitrogen content. Moreover, more the phosphoric acid added, higher the ammonium nitrogen content was. The results of anova showed that the difference between treatments was extremely significant ($F=5.38$, $P=0.009$). At the end of the test, compared with the same proportion of superphosphate treatment, the ammonia nitrogen content of the $\text{Mg}(\text{OH})_2+\text{H}_3\text{PO}_4$ treatment increased by 0.75, 2.98 and 3.92 $\text{g}\cdot\text{kg}^{-1}$ DM with the increase of the addition proportion respectively. This was because the fixing agent combined with ammonium nitrogen to produce magnesium ammonium phosphate. On the one hand, this not only could control nitrogen loss, but also could produce a high-quality slow-release fertilizer, which was more potential than the former two.

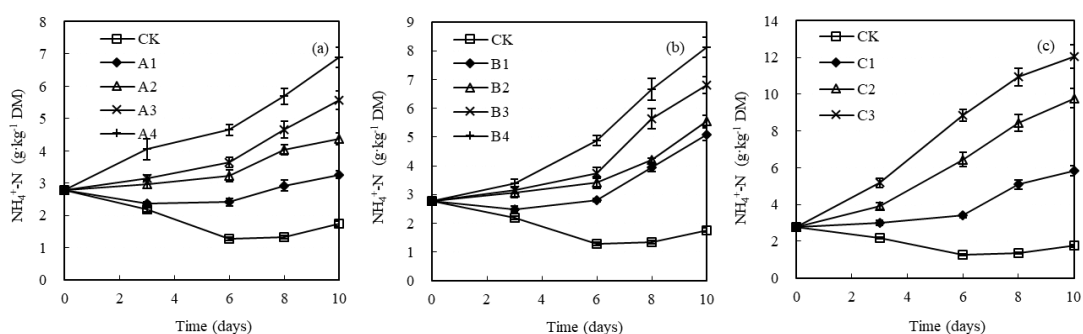


Fig 5 $\text{NH}_4^+\text{-N}$ changes of different treatments during simulated composting (a) peat, (b) superphosphate, (c) $\text{Mg}(\text{OH})_2+\text{H}_3\text{PO}_4$. CK, control; A1, 3.85% peat; A2, 5.66% peat; A3, 7.41% peat; A4, 9.09% peat; B1, 3.85% superphosphate; B2, 5.66% superphosphate; B3, 7.41% superphosphate; B4, 9.09% superphosphate; C1, 3.85 $\text{Mg}(\text{OH})_2+\text{H}_3\text{PO}_4$; C2, 7.41% $\text{Mg}(\text{OH})_2+\text{H}_3\text{PO}_4$; C3, 9.09% $\text{Mg}(\text{OH})_2+\text{H}_3\text{PO}_4$

3.2.4 Nitrogen fixation rate

At the end of composting, the nitrogen loss rate of the control treatment was 55.72%. The change of nitrogen fixation rate of different treatments was shown in figure 6. As could be seen from the figure, the nitrogen fixation rate of each additive increased with the increase of the additives. In addition to C1 treatment, the treatment of $\text{Mg}(\text{OH})_2+\text{H}_3\text{PO}_4$ showed the best nitrogen fixation effect, and the treatment with the 9.09% amount of the addition had the highest nitrogen fixation rate (being up to 66%), followed by superphosphate and peat treatment.

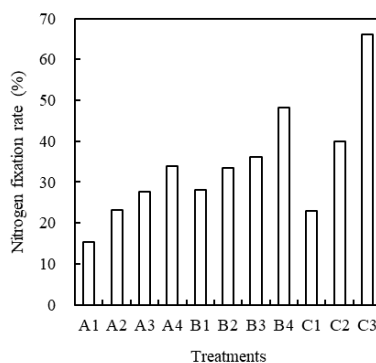


Fig 6 Ratio of nitrogen fixation of different treatments A1, 3.85% peat; A2, 5.66% peat; A3, 7.41% peat;

A4, 9.09% peat; B1, 3.85% superphosphate; B2, 5.66% superphosphate; B3, 7.41% superphosphate; B4, 9.09% superphosphate; C1, 3.85 Mg(OH)₂+H₃PO₄; C2, 7.41% Mg(OH)₂+H₃PO₄; C3, 9.09% Mg(OH)₂+H₃PO₄

4. Conclusions

1) It was feasible to simulate the process of aerobic composting with constant temperature water bath in the laboratory.

2) Peat, superphosphate and Mg(OH)₂+H₃PO₄ affect the nitrogen form and conversion by changing the nature and biochemical reaction during the process of composting, and thus inhibited the ammonia volatilization to different degree. Furthermore, within a certain range, with the increased of the addition ratio, the better the fixation effect on ammonia nitrogen was, the less the ammonia volatilization was, the higher the ammonium nitrogen and the total nitrogen content were.

3) Under the same simulated composting conditions, the nitrogen fixation effect of the three kinds of fixatives with the same proportion was as follows: Mg(OH)₂+H₃PO₄ > superphosphate > peat. The fixation effect of nitrogen increased with the increase of the additives. The nitrogen fixation rate of Mg(OH)₂+H₃PO₄ treatment was up to 66%. Compared with the control group, the amount of cumulative ammonia volatilization decreased by 90.3% and the total nitrogen content increased by 39.31% in this treatment. Compared with other two kinds of fixing agent, Mg(OH)₂+H₃PO₄ could not only control nitrogen loss in composting process, improve the nitrogen nutrient content of compost, but also could increase phosphorus and magnesium nutrients. Therefore, it had more popularization value and application prospect.

Acknowledgements

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