APPLICATION OF NATURAL ZEOLITES FOR THE REDUCTION OF AMMONIA EMISSIONS DURING THE COMPOSTING OF ORGANIC WASTES IN A LABORATORY COMPOSTING SIMULATOR

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Abstract

Ammonia losses from composting of unchoppped and chopped straw–pig slurry mixtures were studied in a laboratory composting simulator. Ammonia emissions were reduced when pig slurry was composted with chopped straw. Chopped straw was more easily degraded by the microorganisms because its surface area was higher than that of the unchopped straw. An average of 84·88% of initial NH_4-N was immobilized and incorporated into the organic-N fraction.

Zeolite clinoptilolite was very effective in trapping the ammonia lost during the composting process. The zeolite sample was placed inside the composting simulator, in the spent-air stream, just after the air had passed through the composting material. Reduction in the effectiveness of ammonia adsorption in zeolites was related to their water adsorption. The concentration of ammonia in the airstream played an important role in the ammonia adsorption. The zeolite amount required to retain 80% of N-losses was 53 g kg^{-1} of fresh chopped straw–pig slurry mixture, while the amount was 82 g kg^{-1} of fresh mixture when unchopped straw was used. The combination of mixing the pig slurry with an easily degradable straw and covering the composting material with zeolite minerals is a very effective procedure for reducing ammonia emissions.

Key words: Ammonia-volatilization, composting, N-immobilization, straw, zeolite.

INTRODUCTION

Well-aerated composting systems of organic wastes rich in nitrogen compounds easily biodegradable compared to the organic carbon lead to the formation, accumulation and consequential loss of nitrogen, mostly by ammonia volatilization. Different factors affect the ammonia volatilization during composting of organic materials. During the first phase of the process the combination of a high ammonium concentration, high temperatures, and raised pH may lead to great ammonia losses (Witter, 1986). Also, high aeration of the composting piles increases the rate of volatilization of the ammonia formed (Ashbolt & Line, 1982).

Nitrogen losses by ammonia volatilization have been evaluated in different composting materials. Witter and Lopez-Real (1988) found that N-losses could amount to 50% of the initial total-N in composting of sewage sludge–straw mixtures, and during the initial phase between 16 and 24% of total-N was lost. According to Hansen et al. (1989), during composting of poultry manure N-losses were up to 33% of the initial total-N. Composting of raw-limed sludge and woodchips produced an N-loss of approximately 10% of the total-N (Sikora et al., 1983). Losses of 26% of N in the ammonia form were found by Loynachan et al. (1976) in experiments with pig slurry over 83 days. Faassen and Dijk (1979) reported N-losses of 27–41% of the initial total-N during composting of pig slurry–straw mixtures. Ammonia losses up to 40–50% of the total-N were reported by Jakobsen (1988) for the composting of slurry–straw mixtures.

High ammonia losses reduce the agronomical value of the compost, contribute to the pollution of the atmosphere, and affect acid rain production. Due to its high solubility in water, ammonia can return to soil and lakes via rain, modifying the normal nitrogen cycle.

Reducing ammonia losses during the composting of organic wastes is therefore of high priority. Minimizing the ammonia produced in the process, and its collection, require study. The aim of this work was to evaluate nitrogen losses during composting of pig slurry–straw mixtures, using a laboratory composting simulator. The effectiveness of different natural zeolites and sepiolite minerals as ammonia adsorbents for the composting process was also studied.

METHODS

Laboratory studies were conducted using an adiabatic laboratory composting simulator. The simulator was

similar to that described by Witter and Lopez-Real (1988). It consisted of a waterbath containing an airtight, anodized aluminium vessel, in which a plastic 5-litre bucket was placed containing the pig slurry–straw mixture. Air was forced through a port in the bottom of the plastic container and diffused by a plate placed immediately above the port and 6 cm below the wire mesh supporting the composting material. Effluent air was drawn from the top of the plastic bucket and cooled in a condenser. Effluent air was passed to an acid scrubber solution to remove ammonia.

The required amount of fresh pig slurry and unchopped or chopped wheat straw as bulking agent were mixed together in different weight ratios (1:4, 1:4·5, 1:4·3 straw:slurry). The mixture was left for 48 h, with occasional mixing, so that the slurry could be absorbed by the straw. Then the material was placed inside the composting simulator for composting. The average lengths of the unchopped and chopped straw were respectively 30 and 6 cm (bulk density 0·05 and 0·073 g cm^{-3}). Aeration was controlled according to the demand necessary to hold the desired operating temperature. The temperature differential between the slurry–straw mixture and the external bath was set at 0·5°C.

Two different zeolites clinoptilolites and one sepiolite were used as ammonia-adsorbent materials. Their adsorption capacities had been studied previously (Bernal & Lopez-Real, 1992). The adsorbent materials were situated in a plastic tube inside the composting simulator, in the spent airstream just after the air passed through the composting material. The adsorbing materials were placed inside the simulator in order to maintain them at the same temperature as the composting material and to prevent their saturation with condensed water.

Tables 1 and 2 show the composting conditions, and the analysis of the materials used in each trial. Trials 4 and 5 were replicates. Moisture content of the materials was calculated after drying at 105°C. Total nitrogen was determined by a Kjeldahl method (Bremner, 1965). Ammonium nitrogen was determined colorimetrically (Krom, 1980) after extraction of the fresh sample with 2M KCl (1:20). For the slurry and the end material the colour of the KCl extract was removed with charcoal. Ammonia loss was evaluated by acid titration of the 2% H_3BO_3 scrubber with methyl red and bromocresol green mixture as an indicator. Nitrate content in the material after composting was determined in water extraction followed by colorimetric analysis with sulphanilamide, after reduction to

Table 1. Description of the composting conditions in each trial

Trial	Materials[a]	Ratio	Fresh weight (g)	Maximum temperature (°C)	Days of composting
1	S + PS	1:4	703·15	45	13
2	S + PS	1:4·5	867·15	45	6
3	CS + PS	1:4·3	1060·00	45	17
4	CS + PS	1:4·3	1060·00	55	15
5	CS + PS	1:4·3	1060·00	55	15
6	S + PS	1:4·3	810·00	45	15

[a]S = straw; PS = pig slurry; CS = chopped straw.

Table 2. Nitrogen balance in the different composting trials

	Trials					
	1	2[a]	3	4	5	6
Initial materials						
Dry matter (%)	18·47	15·26	16·82	16·79	16·79	17·38
Total-N (% dry matter)	1·61	1·86	1·12	1·07	1·07	1·29
NH_4-N (% dry matter)	0·65	1·06	0·49	0·44	0·44	0·42
End materials						
Dry matter (%)	ND	23·20	31·65	26·17	22·12	32·52
NH_4-N (% dry matter)	ND	0·734	0·012	0·021	0·009	0·001
NH_4-N loss						
% total-$N_{initial}$	7·93	14·86	4·95	5·81	6·15	13·47
% NH_4-$N_{initial}$	19·59	26·06	11·42	14·26	15·11	41·00
N-immobilization						
% NH_4-$N_{initial}$	ND	17·89	86·90	82·99	84·76	58·81

[a]N-immobilization calculated from the total-N content in the end sample in this trial only.
ND = not determined.
NO_3-N concentration in the end materials was always negligible.

nitrite with hydrazine (Henriksen & Selmer-Olsen, 1970). Analyses were done in triplicate.

RESULTS

According to the results of the different trials presented in Table 2, the ammonia loss was influenced by various factors: the ratio straw/slurry, the type of straw and the temperature.

Higher proportions of slurry in the mixture increased the N-volatilization. The maximum N-loss was 15% of total-N of the initial mixture, corresponding to 26% of NH_4-N. Addition of chopped straw to pig slurry reduced the ammonia loss to 4·95% of total-N, or 11·4% of NH_4-N. That means a reduction in N-loss of 8·52% of total-N, or 29·58% of NH_4-N. Increasing the maximum composting temperature from 45 to 55°C in samples of slurry and chopped straw mixtures only caused an increment in ammonia loss of 1% of the total-N; an average of 14·69% of the NH_4-N was lost at 55°C. Nevertheless, the N-losses during composting of pig slurry with unchopped straw at 45°C were higher than those with chopped straw at 55°C. This means that the maximum temperature of composting did not have an important effect on the NH_4-N loss, the straw size was the most important factor.

Nitrogen immobilization was calculated from the N-loss and NH_4-N concentration in the initial and end materials:

$$NH_4\text{-}N_{immobilization} = NH_4\text{-}N_{initial}$$
$$-(NH_4\text{-}N_{end} + NH_4\text{-}N_{loss})$$

Since nitrate concentrations in the end materials were negligible, nitrification did not start in the 15 days of composting. The lower ammonia volatilization in chopped straw–pig slurry mixtures caused an ammonium immobilization in the range of 86·9–84·8% of the initial NH_4-N in the mixture, much higher than the 58·81% of initial NH_4-N immobilized in the experiment with unchopped straw under the same composting conditions (trial 6). Chopped straw increased the inorganic-N immobilization to an average of 27·04%. Temperature did not have any significant effect on the

ammonium immobilization since similar values were observed in both trials with chopped straw at different composting temperatures.

Two zeolite clinoptilolites and one sepiolite were used as ammonia adsorbents. The amount of zeolite to be used was calculated according to the ammonia-adsorption capacities of the materials determined previously (Bernal & Lopez-Real, 1992) and the expected ammonia loss from the compost system. Different amounts of the same zeolite were also tested in order to study any change in the effectiveness of the zeolite (Table 3).

Ammonia adsorption in the zeolite ranged from 0·74 to 2·40 mg N g^{-1}, and a lower value was obtained in sepiolite. As the ammonia was retained in the materials, water was also adsorbed ranging from 0·085 to 0·277 g H_2O g^{-1}. Due to these two parallel adsorption processes, the effectiveness of the materials in trapping ammonia was greatly reduced, according to the adsorption capacity calculated previously (Bernal & Lopez-Real, 1992). The reduction in effectiveness (RE) of the zeolite in trapping ammonia was calculated according to the ammonia-adsorption capacity and the amount of ammonia trapped in the composting simulator:

$$RE = 100 - (100 \, NH_3\text{-}N \text{ trapped}/$$
$$NH_3\text{-}N \text{ adsorption capacity})$$

The minimum reduction was 61·66% of ammonia-adsorption capacity. A regression equation between the reduction in effectiveness in trapping ammonia and water adsorption was found, including the three materials:

$$RE = 126·20\,W + 52·918; \quad r = 0·9796**$$

where RE is the reduction in effectiveness (%), and W is the water adsorbed in the material (g H_2O g^{-1}). Results from trial 4 were not included, because a technical fault resulted in the aeration being continuous during the last 24 h. The excess of air could have altered the final water content of the zeolite.

More that 90% of the N-loss was trapped in 88 g of zeolite-1. Nevertheless, the retention of ammonia (% of

Table 3. Effectiveness of the zeolites in trapping ammonia from a laboratory composting simulator

Trial	Zeolite used			Adsorption in zeolite after composting		N trapped (% N-loss) (%)	Reduction in effectiveness (%)
Trial	Type[a]	Weight (g)	Adsorption capacity[a] (mg N/g)	H_2O (g/g)	NH_3-N (mg N/g)		
1	Z1	88	10·10	0·255	1·76	93·50	82·56
2	S	100	4·55	0·265	0·56	15·38	87·63
3	Z3	10	6·26	0·277	0·74	7·46	88·20
4[b]	Z3	30	6·26	0·100	1·46	39·40	76·67
5	Z3	48	6·26	0·133	1·71	69·84	72·63
6	Z3	80	6·26	0·085	2·40	78·63	61·66

[a]Z1, zeolite-1; S, sepiolite; Z3, zeolite-3, their characteristics were described in Bernal & Lopez-Real (1992).
[b]Due to a technical fault, aeration was continuous during last 24 h.

N-loss) increased sharply with the amount of zeolite in trials with chopped straw. About 53 g of zeolite-3 per kg of composting material may be used to retain 80% of N-loss, while in mixtures with unchopped straw the amount of zeolite needed was higher ($82 \, g \, kg^{-1}$).

DISCUSSION

Ammonia volatilization from a composting system depends on the carbon source for the microorganisms. When a labile carbon source is being degraded by microorganisms, the inorganic nitrogen is incorporated into organic forms due to growth of the microbial population. Part of the unchopped straw may be physically inaccessible to degradation by microorganisms, the process of decomposition may start on the surface of the materials. Cheshire et al. (1979) suggested that the decomposition process of the straw may coat the surface with an impenetrable humified layer. Chopped straw, with a higher surface area, was more easily degradable by the microorganisms than unchopped straw. Its more-available carbon caused the immobilization of the inorganic nitrogen added in the slurry, resulting in the incorporation of an important part of the NH_4-N into the organic-N fraction.

Increasing the proportion of slurry to straw increased the ammonia losses, due to the high initial level of NH_4-N. Faassen and Dijk (1979) reported increases in N-loss with the amount of NH_4-N present at the start. They also found incorporation of inorganic-N into organic forms during the composting of pig slurry with straw. Morisaki et al. (1989) indicated that ammonia volatilization during sewage-sludge composting could be reduced by increasing the amount of rice husks as a bulking agent. The same authors also found little change in the total-N of the composting material. The reason was that the ammonia produced was trapped in organic and exchangeable NH_4-nitrogen forms.

The ammonia-adsorption capacity of the zeolite and sepiolite minerals was greatly reduced compared to theoretical values, when both were used in the composting simulator. Higher water retention in zeolites and sepiolite occurred at 45°C, relating to the higher water losses at this temperature. A linear relationship was found between the reduction in effectiveness and the water adsorption. This indicated that the water adsorbed in these materials blocked their internal channels against the ammonia adsorption. Hayhurst (1978) suggested this idea for zeolite phillipsite exposed to a mixture of water vapour and ammonia gas. Zeolite clinoptilolite may have a high capacity for water adsorption, due to its bigger kinetic pore diameter than the phillipsite, and a competitive effect between the water and ammonia molecules could result. The water loss in the composting process is a very important factor in determining the effectiveness of the zeolite in trapping ammonia, and consequently the amount of zeolite needed.

The amount of nitrogen adsorbed per gram of zeolite was greater with mixtures of pig slurry and unchopped straw than with chopped straw. This was also a consequence of the higher ammonia concentrations in the airstreams from the unchopped straw than from the chopped straw, because of the higher N-losses. The ammonia adsorption in zeolites follows a Langmuir equation model; their capacity to adsorb ammonia increases with the gas concentration in the atmosphere. However, the amount of zeolite necessary to retain the same proportion of ammonia loss was higher in the composting system with unchopped straw. Since the highest N-loss occurs during the composting of unchopped straw-pig slurry mixtures, the amount of zeolite should be more than 150% of the amount used in mixtures with chopped straw, if the same proportion of ammonia loss has to be avoided.

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