REDUCING AMMONIA LOSSES BY ADDING $FeCl_3$ DURING COMPOSTING OF SEWAGE SLUDGE

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Abstract. The release of ammonia nitrogen during composting of sewage sludge mixed with a lignocellulosic bulking agent leads to a reduction in the agronomic value of the final compost and to harmful effects on the environment. We propose adding a cheap salt $FeCl_3$ which can be used without special precaution to reduce ammonia losses by decreasing pH conditions. An in-vessel co-composting experiment was conducted in a large reactor (100 L) in which $FeCl_3$ was added to sludge mixed with a bulking agent (pine shavings and sawdust) and compared with a control mixture without $FeCl_3$. Temperature, oxygen consumption and pH were monitored throughout the composting of both mixtures. The final balance of organic matter, organic and inorganic nitrogen permitted to conclude that the addition of $FeCl_3$ reduced nitrogen loss (by a factor of 2.4 in relation to the control) and increased mineralisation of the organic nitrogen by 1.6.

Keywords: ammonia, composting, iron chloride, nitrogen, sewage sludge, volatilization

1. Introduction

All over the world, municipal wastewater treatment plants are on the increase and the processes used are improving. As a result such plants are producing greater and greater amounts of sewage sludge. In 1990 the United States generated approximately 6.2 10^6 dry metric tons (Mg) (Hue,1995) while the European community produced around 7 10^6 Mg (Guiresse *et al.*, 1995). These figures might attain 12 10^6 in U.S. and 17 10^6 in Europe by the year 2000. It is thus becoming urgent and necessary to establish a suitable protocol to deal with the fate of such products. The wide use of land application could permit recycling of the nutrient elements. However this practice will require environmental precautions and treatment to dehydrate and stabilize the raw sludge.

Composting might provide an easy and cheap treatment resulting in a stable, hygienic and more valuable endproduct for crops (Baldoni *et al.*, 1996). Exothermal biological oxidation is carried out by different groups of aerobic micro-organisms. Sludges are nitrogenous materials with high moisture contents and in addition to a forced input of air or oxygen, gaseous circulation within the mass has to be facilitated to maintain a permanent state of aerobiosis. Sludges are therefore mixed with suitable proportions of bulking agent such as lignocellulosic materials (wood shavings or sawdust, for example) which absorb the moisture and increase porosity for aeration. (Haug, 1993).

Sludges are also rich in proteins, urea and uric acid, and high amounts of ammonium are released by enzymatic hydrolysis (Mathur, 1991). The micro-organisms which degrade the carbonaceous bulking agent use a fraction of this ammonium for their own metabolism but most is lost by ammonia volatilization (Witter and Lopez-Real, 1987) as producing odour noxious and reducing the agronomic value of the composted endproduct. A similar loss of nitrogen also occurs when animal manure is stored and after application to the soil. Ammonia volatilization during sludge composting is favoured by circulation of the air (or oxygen) required to maintain aerobic conditions, by a slightly or non-acid pH, high temperature and high nitrogen to carbon ratio (Bishop and Godfrey, 1983).

Few solutions have been found to prevent the release of ammonia into the atmosphere and wastage of a valuable agricultural resource. The commonest solution is to increase the C/N ratio with bulking agents which are also used as carbonaceous amendments (Morisaki *et al.*, 1989). However encrustation of the cellulose fibrils with lignin (Whitney and Lynch, 1996) makes the lignocellulose recalcitrant to biodegradation (Chahal, 1991) and ammonification often goes beyond the needs of the micro-organisms. Witter and Lopez-Real (1988) suggested placing a layer of zeolite (clinoptilolite) on top of the composting material to trap the ammonia. High level (30%) of zeolite must however be used to reduce the ammonia volatilization effectively. Unfortunately this silicate is not always available and cannot be commonly used in composting. Another solution is to decrease the pH during composting as managers of animal manure do before spreading cow or pig slurries (Stevens *et al.*, 1989).

In this work, we propose reducing ammonia loss through the acidifying action of iron chloride ($FeCl_3$) (Boucher, 1996). This product is particularly inexpensive, and could therefore be used on an industrial scale. As $FeCl_3$ is also an industrial waste, it could thus be recycled. The aim of this paper was to assess the acidifying action of $FeCl_3$ and its effectiveness in preventing ammonia loss during the composting of sludge. We also wanted to check that the $FeCl_3$ did not exert any inhibiting effect during composting. Two sludges and their mixture with a lignocellulosic bulking agent were therefore characterized and in-vessel composted with and without $FeCl_3$. The composting processes were monitored and the endproducts analyzed to compare the quality of both composts.

TABLE I

Physicochemical characteristics of two urban sludges expressed in relation to dry (∗) or fresh matter (∗∗)

	sludge A	sludge B
Moisture content (%)∗∗	79.4	82.4
Dry matter (%)∗∗	20.6	17.6
pH water	5.8	6.8
Ash (%)∗	16.3	20.3
OM (%)∗	83.7	79.7
TKN (%)∗	5.8	7.2
C/N	7.2	5.5
CaO (g/kg)∗	10.22	23.50
K_2O (g/kg)∗	1.31	3.75
MgO (g/kg)∗	1.72	5.35

2. Materials and Methods

2.1. ANALYTICAL TECHNIQUES

The dry matter (DM) of sludge and mixtures before and after composting was obtained by heating at 105°C to constant weight and the organic matter (OM) by calcination for 8 hours at 480°C (AFNOR, 1991). The total nitrogen (TKN) was determined by Kjeldahl method (Stevenson, 1982). The ammonium and nitrates were extracted from the fresh matter with hot water at 90°C then assayed by colorimetry: NH_4 after reaction with phenol in the presence of hypochlorite (Charlot, 1961) and NO_3 as described by Kamphake (1967). Organic nitrogen content (ORGN) was deduced by difference: ORGN = TKN – NH_4 (Stevenson, 1982). The pH was measured in a suspension of fresh matter in H_2O, 1w/2v, after 10 minutes on a shaker (AFNOR, 1987). Ca, K and Mg were assayed by atomic absorption spectrophotometry, after calcination (480°C) and taking up the ashes in HCl (AFNOR, 1987).

2.2. SLUDGE SAMPLES AND ACIDIFICATION

Two urban sewage sludges were used in succession. Both had high moisture and nitrogen contents (Table I). The C/N ratios were very low and were expected to induce excessive ammonification. The mineral elements Ca, Mg and K occurred in sufficient amounts to ensure the good nutrition of the micro-organisms. The two test sludges differed in pH. Sludge A the most acid (pH = 5.80) was used as control.

Sludge B was practically neutral (pH = 6.80) and was acidified by adding $FeCl_3$ as a commercial technical grade in a 2.55M solution.

Since the optimal pH for mostly decomposer organisms is between 6.5 and 7.5 (Alexander, 1977) pH value could not be decreased much below 6. Moreover Bacteria do not easily grow below pH4 and the authors of other experiments on animal manure did not work below pH4 (Stevens *et al.*, 1989). The latter pH value was therefore chosen and the quantity of $FeCl_3$ required to reduce the pH of sludge B to 4.0 determined in a preliminary experiment. A mixture of 49 g of raw sludge (8.62 g DM) and 100 ml of distilled water was kept on a shaker and received successive 0.5 ml aliquots of $FeCl_3$.

2.3. THE SLUDGE-BULKING AGENT MIXTURE

The composting process is mainly dependent on moisture content. On the one hand the microbial kinetics will decline if the water content is deficient. On the other hand too much water will prevent the oxygen transfer necessary to aerobic composting. Most authors agree that the optimal moisture content is about 60–65% (Haug, 1993). As the sludge moisture contents were about 80% (Table I) they were mixed with a bulking agent (BA) consisting of pine shavings and sawdust (Boucher, 1996) with a mean moisture content of 11.9%, the goal being to attain a final moisture content of about 63% (Table II).

The addition of sawdust and shavings of pine resulted in dilution of the mineralomass of the mixture and a subsequent reduction of the ash and nitrogen content, and a higher C/N ratio. Despite the buffering capacity of the bulking agent the pH of the mixture was slightly reduced to 4.8 (Table II).

2.4. THE COMPOST REACTOR

Single composting runs were carried out in a 100-litre insulated and unheated pilot reactor (Viel *et al.*, 1987). The temperature inside the reactor was continuously monitored. Air was forced through the system with a small pressure gradient. Water was trapped at the outlet reactor and the effluent gas sent to a sampling chamber and analyzed for O_2, CO_2 and NH_3. Air circulation had to be reduced to a minimum to avoid any resulting decrease in temperature. The oxygen content of the effluent gas was maintained in the 1–3% range and used for automated control of the aeration of the substrate to suppress any risk of anaerobiosis. The air flow was adjusted periodically and varied from $8\,l\,h^{-1}\,kg^{-1}$ of the DM at the beginning of composting to $20\,l\,h^{-1}\,kg^{-1}$ of the DM during the most intense phase. Oxygen consumption was calculated from the known oxygen flow-rates and the residual concentration.

The effluent gas was trapped in two successive wash bottles to monitor the ammonia losses. In the first, which was initially empty, condensation of a very high proportion of the water vapour brought in by the air, led to dissolution of some of the gaseous NH_3 released by composting. The second bottle contained a known amount of H_2S0_4 which took up the remaining ammonia (Ezelin *et al.*, 1996). The amount of ammonia nitrogen lost during the composting process was determined from assays carried out on each of these two bottles.

Composting was stopped when the temperature in the middle of the mixture was equal to that of the ambient temperature.

2.5. DATA TREATMENT

The percentage decomposition of the organic matter (OMPD) was calculated from the ash amount which was the only constant constituent during composting since the dry matter content decreased between the initial mixture (DM_0) and the end-product (DM_1). OMPD was given by the formula (1).

$$\text{OMDP (\%)} = [100\ (A_1 - A_0)/(A_1(100 - A_0))]\ 100 \qquad (1)$$

with A_0 = % of ash in the initial dry matter and A_1 = % of ash in the final dry matter. In order to study the fate of nitrogen, the degradation of the organic matter had also to be taken into account and the results related to the initial dry matter. The formula (2) was used to relate the final nitrogen content measured in DM_1 (N_{11}) to DM_0 (N_{10}).

$$N_{10} = N_{11}\ A_0/A_1 \qquad (2)$$

with N = NTK, ORGN or NH_4.

To assess the fate of nitrogen during composting, the balance of nitrogen was calculated and measured as follows. The differences between the final (NTK_{10}) and initial (NTK_0) total nitrogen contents gave the nitrogen losses that occurred during composting (LNTK). The differences between the final ($ORGN_{10}$) and initial ($ORGN_0$) organic nitrogen contents gave the ammonified organic N (AORGN). Similarly the differences between the final ($NH4_{10}$) and initial ($NH4_0$) ammonium nitrogen contents gave the ammonium nitrogen fixed in the compost (FNH4). At the same time ammonia volatilization was directly measured in the wash bottles at the compost reactor outlet and expressed in nitrogen as a percentage of the initial dry matter composted (NH3L). Due to the large dimension of the pilot reactor large amounts of sludge (about 10 kg) could be composted in single runs. However the nitrogen was dosed in three replicates and the averages compared with the unilateral Student Test. Results are given when T_{obs} was greater than T_{crit} at a level of 0.05.

3. Results and Discussion

3.1. EFFECT OF ACIDIFICATION ON THE COMPOSTING PROCESS

First of all, the pH of the sludge was gradually decreased to pH4 when 5.86 mmoles

TABLE II

Amounts of organic mixtures composted (sludge+bulking agent (BA)) and their composition before and after composting, expressed in relation to dry ($*$) or fresh matter ($**$) and decomposition percentage of organic matter (OMDP)

	Initial mixtures		Mixtures after composting	
	sludge A + BA	sludge B + BA + $FeCl_3$	sludge A + BA	sludge B + BA + $FeCl_3$
sludge/BA (%)$**$	74/26	73/27		
Total fresh matter (kg)	27.8	30.5	23.0	26.5
Total dry matter (kg)	10.7	10.9	8.6	9.4
Moisture content (%)$**$	61.7	64.2	62.5	64.5
Dry matter (%)$**$	38.3	35.8	37.5	35.5
pH water	5.7	4.8	8.8	8.0
Ash (%)$*$	6.9	9.0	7.7	10.3
OM (%)$*$	93.1	91.0	92.3	89.7
Carbon (%)$*$	46.6	45.5	46.2	44.9
TKN (%)$*$	2.8	2.5	2.7	2.6
C/N	16.6	18.4	17.4	17.0
NH_4-N (g/kg)$*$	6.74	5.20	8.89	13.52
NO_3-N (g/kg)$*$	0.67	0.52	0.13	0.07
OMDP (%)$*$			11.6	14.1

$FeCl_3$ were mixed with 8.62 g of sludge DM (Figure 1). This concentration of $FeCl_3$ was then tested in the composting experiments.

The parallel plotting of O_2 and temperature evolution (Figure 2) displayed a classic pattern during both composting runs. In a first step, the temperature increased greatly in both mixtures. The control mixture (Figure 2A) attained 45°C within 24 h and rose to 72.5°C in 72 h, when the oxygen consumption attained 2.56 $l\ h^{-1}\ kg^{-1}$ DM. In the acidified test sample (Figure 2B), the temperature of 45°C was only attained after 66 h. It took 6 days to attain the maximum. In both cases this high temperature showed that the composting was intensely thermophilic. This step generally requires much attention from the sludge managers because it allows the thermal destruction of pathogenic micro-organisms (Jimenez and Garcia, 1991). However, these temperature conditions were above those required for nitrification (Bishop and Godfrey, 1983; Bhargava and Datar, 1989). As a result the NO_3 contents weres always very low (negligible) in both sludge A and in sludge B. Although acidification of the sludge with $FeCl_3$ delayed the thermophilic stage, it did not prevent the onset of composting and the rise in temperature. In contrast the final OMDP was higher in sludge B than in sludge A (Table II) meaning that

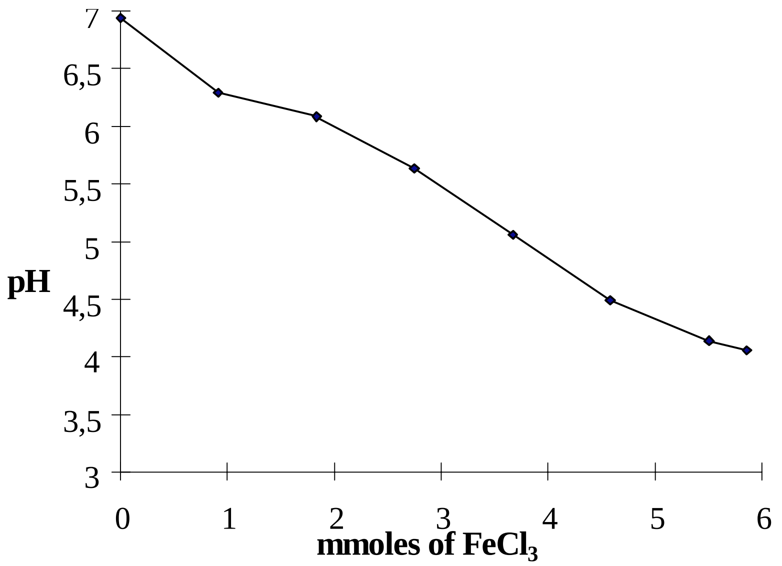

Figure 1. Acidification of urban sludge.

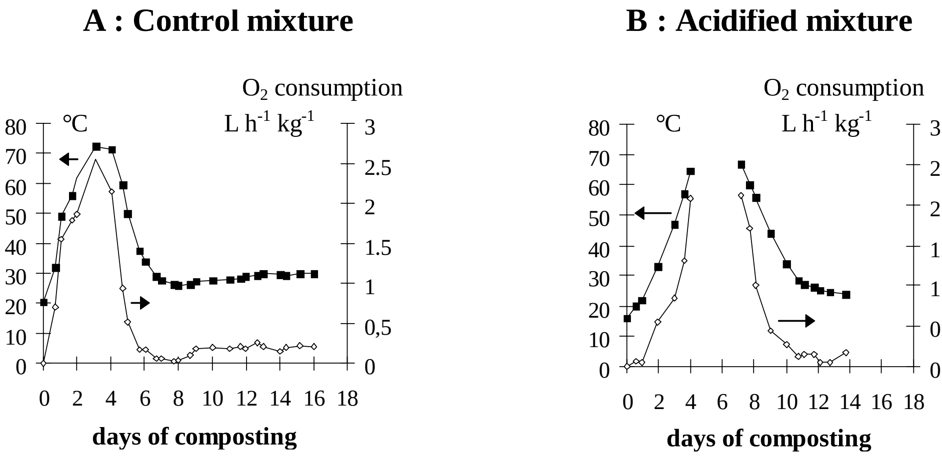

Figure 2. Plot of temperature and oxygen consumption during composting in control mixtures and when acidifed with $FeCl_3$.

acidification delayed the composting process without disturbing it. In a second step the temperature quickly decreased to 30°C in 2 days for sludge A and in 4 days for sludge B. At the same time the oxygen consumption remained around 0.2 l $h^{-1}kg^{-1}$ DM. The microbial activity then decreased considerably indicating thus a stabilized state had been reached as the mesophilic micro-organisms were active.

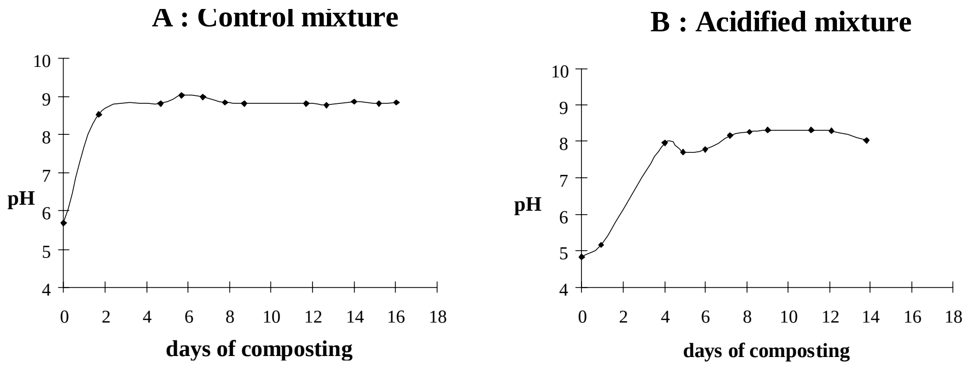

Figure 3. Variation of pH during composting in the control mixture and when acidified with $FeCl_3$.

Throughout both composting runs of the control and acidified sludge mixtures alkalinisation due to the release of NH_4 by the micro-organisms was observed, as described by Atchley and Clark (1979) and can be described as follows(3).

$$C_5H_7NO_2 + 5O_2 \longrightarrow 5CO_2 + NH_4{}^+ + OH^- + H_2O \quad (3)$$

In Equation (3), $C_5H_7NO_2$ was assumed to be the component formula of an activated sludge cell by Matsuda *et al.* (1988). In our experiment the pattern of alkalinisation during composting was not the same for both composting runs (Figure 3). In the case of the non acidified sludge A (Figure 3A), ammonification was immediately apparent and led to rapid rise in pH during 2 days until a maximum concentration of OH^- was attained after which volatilization occurred according to (4).

$$NH_4^+ + OH^- \longrightarrow NH_3 + H_2O \quad (4)$$

In the case of the acidified sludge B, ammonification was delayed probably due to difficult pH conditions for micro-organisms as found by Nakasaki *et al.* (1993). Nevertheless this delay only lasted for a few hours after which the ammonium released produced a pH increase for 2 more days than in the control. $FeCl_3$ probably enhanced the buffer capacity of the mixture due to the following reaction (5).

$$3(NH_4^+ + OH^-) + FeCl_3 \longrightarrow Fe(OH)_3 + 3\,(NH_4Cl) \quad (5)$$

3.2. EFFECT OF ACIDIFICATION ON AMMONIA LOSSES

First of all the nitrogen losses calculated during the composting (LNTK) of sludge A greatly exceeded those of sludge B (Table III) according to the unilateral Student test. The same conclusion could be drawn from the values obtained by direct assay of the wash bottles at the compost reactor outlet (NH3L). Either the calculated (LNTK) or the measured (NH3L) losses were similar (Table III), thus confirming the validity of the assumption that nitrification was actually negligible.

TABLE III

Volatilization assessed by calculated balance (LNTK) and measurement (NH3L) during composting of control and acidified sludge mixed with bulking agent (BA)

	sludge A + BA	sludge B + BA + $FeCl_3$
BEFORE COMPOSTING		
TKN_0	2.81	2.48
$ORGN_0$	2.13	1.96
$NH4_0$	0.67	0.52
AFTER COMPOSTING		
TKN_{10}	2.37	2.30
$ORGN_{10}$	1.57	1.12
$NH4_{10}$	0.79	1.18
Calculated balance (% DM_0)		
$LNTK = NTK_{10} – NTK_0$	–0.44	–0.18
$AORGN = ORGN_{10} – ORGN_0$	–0.56	–0.84
$FNH4 = NH4_{10} – NH4_0$	0.12	0.66
Measurements		
NH3L	–0.55	–0.18

During composting, the total Kjeldhal nitrogen content in the control mixture decreased from 2.81 to 2.37% of initial dry weight and from 2.48 to 2.30% in the treated sludge, i.e. a drop of 0.44% in one and 0.18% in the other (Table III). This reduction, expressed as a % of the initial TKN, was 16% and 7% respectively. Thus the loss corresponding to the ammonia carried in the circulating air was reduced 2.3 times by the addition of $FeCl_3$.

At the same time, the fraction of organic nitrogen decreased from 2.13 to 1.57% of the initial dry weight in the control and from 1.96 to 1.12 in the acidified sludge mixture, i.e. a reduction of 0.56 in the control and 0.84 in the treated mixture. The values, expressed as a function of the initial organic nitrogen, were 26% and 43%, respectively. Ammonification occurred in both cases but was enhanced by a factor of 1.6 in the acidified sample. This would probably be related to the slow increase in pH and the lower maximum pH attained in the treated sludge than in the control which rapidly became too alkaline as Nakasaki *et al*. (1993) had found that the optimum pH for the growth and protein degradation activity of the micro-organisms was in the range of 7–8. Consequently, the percentage degradation of organic matter was also much higher in the treated sludge mixture (Table II).

The ammonium nitrogen rose in the control from 0.67 to 0.79% of the initial dry weight, and from 0.52 to 1.18% in the treated mixture, i.e. an increase of 0.66. These increases expressed as a function of the initial organic nitrogen were 6% and 34% respectively. Thus in both cases fixation of the NH_4 released by ammonification occurred, but this fixation was 5.6 times greater in the treated mixture because of the significant proportion of NH_4 which reacted with Cl according to (5).

4. Conclusion

The addition of $FeCl_3$ to urban sewage sludge (10% w/w) enabled the pH to be decreased from 6.8 to 4. The acidified sludge was mixed with sawdust and shaving of pine and then in-vessel composted. The acidification induced a brief delay in the intense thermophilic phase, but as this microbial activity released ammonium ions and brought about an increase in pH, the medium became progressively more favorable again and microbial activity increased. The thermophilic phase occurred when the pH was between 7 and 8. The presence of $FeCl_3$ later stabilised the pH at a lower value than that attained in the control. In consequence the total microbial activity in the treated mixture was increased, this being apparent as a slightly higher percentage degradation of the organic matter (14.1 compared with 11.6%) and above all, as much higher total ammonification (43 compared with 26% of initial N). At the same time the $FeCl_3$ strongly reduced the loss of ammonia. The amount of NH_3-N lost in our experiment was assessed by calculation: 19g compared with 47g in the non acidified run and by measurement: 19g compared with 59g. This is a very positive point firstly, because the quality of a product that could be used as an organic amendment was thereby improved and, secondly, the harmful effects that a large installation might have on its surroundings were reduced.

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