Compost quality Management by Adding Sulfuric Acid and Alkaline Wastewater of Paper Mill as two Amendments

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Abstract—In composting process, N high-organic wastes loss the great part of its nitrogen as ammonia; therefore, using compost amendments can promote the quality of compost due to the decrease in ammonia volatilization. With regard to the effect of pH on composting, microorganisms' activity and ammonia volatilization, sulfuric acid and alkaline wastewater of paper mill (as liming agent with Ca and Mg ions) were used as compost amendments. Study results indicated that these amendments are suitable for reclamation of compost quality properties. These held nitrogen in compost caused to reduce C/N ratio. Both amendments had a significant effect on total nitrogen, but it should be used sulfuric acid in fewer amounts (20 ml/kg fresh organic wastes); and the more amounts of acid is not proposed.

Keywords—Compost, Paper mill wastewater, sulfuric acid, Ammonia Volatilization.

I. INTRODUCTION

HIS is a well known fact that composting is one of the I most suitable ways of converting organic wastes into more stable products which are safe and beneficial to plant growth, as well as an environmentally friendly and economical alternative method for treating solid waste. Composting is a biochemical process converting various components in organic wastes into relatively stable humuslike substances that can be used as a soil amendment or organic fertilizer. Even though composting is a proventechnology that can be applied on the spot, there are many aspects that should be improved in the performance of current composting facilities. One of these areas is the conservation and enhancement of the nutrients value of the product by reducing the loss of nitrogen [1]. The decreased ammonia loss may lead to an alleviation of the odor problem that is usually encountered in full-scale composting facilities [2]. Ammonia (NH₃) is generated from decomposition of nitrogenous material, i.e. proteins and amino acids.

Ammonia emission frequently occurs during the thermophilic stage of aerobic decomposition and tends to be

high with low C/N ratio. Several factors such as C/N ratio, temperature, mixing and turning and aeration rate can influence the volatilization of ammonia during composting [3]. Gaseous nitrogen losses during composting occur mainly as ammonia, but may also occur as nitrogen and NOx [4]. Witter and Lopez-Real [5] reported that total nitrogen loss could amount to 50% of the initial nitrogen in up to 33% of the initial nitrogen during composting of poultry manure [6].

When different types of organic materials are composted, a higher C/N ratio does not necessarily indicate an effective solution for preventing N loss [4], [7], [8], [9]. Both chemical form and particle size of carbon (C) source affect the availability of C to microorganisms. Glucose, a readily available C source, appeared to cause immediate immobilization of N when an appreciable amount was added to soils [10]. Subair [11] found that glucose was effective in reducing NH3 volatilization from liquid hog manure, whereas material resistant to decomposition (sawdust) was not. Meyer and Sticher [12] showed that N loss during composting of cattle manure and straw could be reduced by increasing the proportion of ground straw to chopped straw whilst maintaining a C/N ratio of 31.6.

In this study, objective is to evaluate the effectiveness of two materials as amendments in reducing N losses and increasing municipal compost quality. These amendments are sulfuric acid as an acidic factor for decrease in organic mass alkalinity and ammonia volatilization; and paper wastewater having Ca and Mg ions for ammonia precipitation. Alkaline wastewater is a by-product of paper mill that is an environmental issue in addition to transportation costs as disposal material; therefore, suitable use of this by-product in amending compost quality decreases these problems.

Alkaline wastewater of paper mill is a by-product of the paper production industry that thousands cubic meter is produced in Talesh-Choka and Haft Tappeh paper factories; and other factories in Iran. This research was designed to investigate the effects of sulfuric acid and paper mill wastewater (from Talesh-Choka factory) respectively as acidic amendment and a lime factor having Ca and Mg ions during March-October 2008. Some properties of the used paper lime wastewater are observed in Table I.

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 TABLE I

 SOME PROPERTIES OF THE USED PAPER MILL WASTEWATER

 Property
 Amount

 pH
 12.75

 EC (dS/m)
 65.0

 CaCO₃(%)
 36.5

Ca (g/kg)

Mg (g/kg)

For providing municipal wastes, the material discharged from the rotary drum was passed through the trommel screen with the finer size fraction being collected through the screen and the coarser size fraction being collected on the screen. The finer fraction contains mainly biodegradable organic materials and was used for composting and the coarse fraction contains mainly non-biodegradable organic (e.g., plastics) and inorganic (e.g., metals, glass) materials was sent to a landfill. The fines account for 50-55% of the original weight of material and have a moisture content of 55-60%. Some properties of the used municipal wastes are observed in table 2. Each of treatments with 20 kg fresh organic wastes (decomposable municipal) in three replicates as a completely randomized design was done.

 TABLE II

 CONCENTRATION OF THE SOME ELEMENTS AND PH IN THE USED MUNICIPAL

	WASTES			
Parameter	Amount	Parameter	Amount	
pH	6.24	Cl (%)	0.51	
(1:6 dry O.M/water)				
N (%)	1.12	Na (%)	0.62	
C (%)	16.27	S (%)	0.24	
P (%)	0.29	Fe (%)	0.70	
K (%)	0.24	Zn (ppm)	302	
Ca (%)	1.86	Mn (ppm)	311	
Mg (%)	0.22	Cu (ppm)	186	

Treatments included different amounts of sulfuric acid and paper lime sludge fully mixed to decomposable organic wastes as following:

Municipal wastes control treatment (A0L0): no amendment

A20 treatment i.e. 20 ml sulfuric acid per 1 kg fresh organic wastes (municipal wastes),

A40 treatment i.e. 40 ml sulfuric acid per 1 kg fresh organic wastes (municipal wastes),

L2 treatment i.e. 2% paper mill alkaline wastewater,

L4 treatment i.e. 4% paper mill alkaline sludge.

Treatments in free space weekly twice to turn upside down for aeration, while exercising some treatments and adding water for adjusting moisture of organic wastes were also done. After 50 days, a 100 g sample of every treatment was taken. The samples were air dried and ground to pass through a 1 mm sieve. Total kjeldahl nitrogen (TKN) and total organic carbon (TOC) of samples were estimated by using a microkjeldahl method [13] and Walkey and Blacks Rapid titration method [14]. The pH and EC were determined on a water extract from compost using compost to water ratio of 1:6 by weight. The pH and EC values were determined from three 5 g samples that for each sample, 30 ml of DD water was added and mixed to compost. Microbiological assays (microbial activity detecting) were done with bacteria, actinomcetes and fungi plate counting method as described by Storm [15]. Actinomycetes and fungi were isolated on the agar plates by dilution plating. Mesophilic and thermophilic microbial strains were obtained by plating samples taken from composting processes and cultivating the plates at 30 and 60°C, respectively [16].

Data were analyzed by standard ANOVA procedures using MSTATC and SAS software and significant differences was determined based on P<0.05 level for the least significant difference Test.

Table III indicates the temperature of the organic wastes during 7 weeks of composting process. In all treatments, the highest temperature of organic masses occurred at the fourth week that increased to more than 50°C excluding 40 ml sulfuric acid treatment. Maximum temperature at recent treatment (A40), 8-10°C is less than in the other treatment. This can be due to the effect of the higher used acid on activity and growth of microorganisms. Table IV shows the total hetrotroph counts in different treatments during the composting (log cfu/g). It is observed that there is conformity between total hetrotroph counts and temperature, so that, more microorganisms population is related to the higher temperature, because the increase in temperature is because of activity and growth of microorganisms.

TABLE III Organic Wastes Temperature (°C) During the Composting Time Different Treatments

Treatments -	Time after composting start (week)						
	1	2	3	4	5	6	7
A_0L_0	32	37	42	51	48	39	28
A ₂₀	27	37	49	52	45	32	30
A_{40}	29	32	46	49	41	35	25
L_2	26	36	45	52	40	33	28
L_4	29	34	47	50	38	32	29

TABLE IV					
TOTAL HETROTROPHS COUNTS IN DIFFERENT TREATMENTS DURING THE					
COMPOSTING (LOG CFU/G)					

Tractments	Time after composting start (week)						
Treatments	1	2	3	4	5	6	7
A_0L_0	6.1	7.4	8.2	9.4	9.3	8.0	6.0
A ₂₀	5.9	6.9	8.1	10.1	10.0	9.0	6.8
A_{40}	6.2	6.4	8.2	8.6	7.9	7.6	7.1
L_2	6.7	7.8	8.9	10.6	10.1	8.1	7.3
L_4	6.1	6.8	9.1	10.5	8.8	8.6	7.0

Table V shows the effect of treatments on the total nitrogen of produced compost. Use of 20 ml sulfuric acid per 1 kg fresh organic wastes (municipal wastes) increased total nitrogen than in the control that can be due to decrease in pH of organic mass. Ammonia volatilization can be stopped by decrease in mass pH (Table V). Experimental data [17], [18] indicated that severe losses of NH3 occurred when high pH values were measured. Inorganic chemicals have been used to inhibit ammonia volatilization by increasing the acidity of compost mixtures [19], [20], [21].

Adding 40 ml sulfuric acid has decreased the total nitrogen of municipal wastes compost. Regarding Table IV, heterotrophs counts in 20 ml sulfuric acid treatments is more than 40 ml sulfuric acid that this can be due to the effect of acid on microorganisms' activity. Carey et al. [19] believed that the addition of sulfuric acid reduces ammonia volatilization, but the low pH may have negative influence on heating process. In present study, it seems the effect of sulfuric acid on microorganisms' activity has a more importance for stopping ammonia than the decrease in mass pH.

TABLE V EFFECT OF THE TREATMENTS ON THE TOTAL N, C, C/N RATIO, PH AND EC

	U	OF I RODUCED	COMPOSI		
treatment	Nitrogen	Carbon	C/N	pН	EC
	(%)	(%)		(1:6)	(1:6)
A_0L_0	0.78 fghi	11.80 cd	15.56 cd	8.11 abcd	6.65 hi
A ₂₀	1.89 b	11.20 d	5.96 g	7.46 f	7.60 ab
A_{40}	0.71 ghi	11.80 cd	17.00 cd	6.95 g	8.06 a
L_2	1.75 c	11.40 cd	6.51 a	8.16 ab	7.52 ab
L_4	2.25 a	11.30 cd	5.02 a	8.23 a	8.06 a

LSD (least significant difference) shows the significant difference ($\rho<0.05$) among the means of treatments.

Values followed by the same letters in each column are not significantly different at the 0.05 level (least significant difference).

Using 2% paper wastewater has significantly increased total nitrogen than in the control. The greatest increase in total nitrogen is related to 4% paper wastewater. For investigation of the paper mill wastewater effects on total nitrogen, we must consider two subjects: 1. Increase in pH of organic mass and 2. Ca and Mg ions of paper mill wastewater. Base on table 5, we don't see considerable change of compost pH in 50 days duration, but the pH measurements at 24 hr after adding paper wastewater denoted to increase in pH (pH was 8.75 and 8.95 for 2% and 4% paper wastewater, respectively). Increase in pH of compost increases ammonia volatilization [1], but the ammonia volatilization is not very important at the primary stages because many organic compounds have still been decomposed. With increase in microorganisms' activity, organic compounds (especially proteins) are gradually decomposed and ammonia is produced, but organic acids are simultaneously produced to reduce pH derived from adding alkaline wastewater (correction of pH). Consequently, wastewater effect on pH and ammonia volatilization decreases during time. Therefore, positive effect of paper mill alkaline wastewater on total nitrogen of final compost can be due to its Ca and Mg ions. Calcium and Magnesium salts have also been added to precipitate ammonia with carbonate and to remove the alkalinity that could prevent a rise in pH [22]. Precipitation of struvite (MgNH₄PO₄.6H₂O) also is a common phenomenon in anaerobic treatment facilities [23]. Jeong and Kim [1] investigated a new method for conservation of ammonia in aerobic composting. They demonstrated that struvite crystals could be formed in aerobic composting, when sufficient Mg and P were added. This crystallization process resulted in a substantial reduction of ammonia loss.

Base on Table V, carbon percent has significantly not changed in different treatments. Therefore, significant differences between C/N ratios of treatments are due to the total nitrogen differences. C/N ratio in 20 ml sulfuric acid treatment and paper mill wastewater treatments is even less than in the control. Although, using sulfuric acid and paper mill wastewater caused to increase electrical conductivity amounted 0.87-1.41 units than control, but we can tolerate this

due to the desirable effects of these materials on total nitrogen and C/N ratio, because when the compost is dispersed in soil, its salinity is adjusted (corrected) by the soil salinity.

II. CONCLUSION

Results indicated sulfuric acid and paper mill wastewater are suitable amendments for increase in the agronomic value of the produced compost quality. But it should be regarded using sulfuric acid is suitable at fewer amount (20 ml/kg fresh organic wastes; decomposable municipal wastes) and more use of that is not proposed. The paper mill wastewater had a more effect on total nitrogen of the produced compost than sulfuric acid. It is proposed to investigate effect of the other amendments such as carbonic amendments on compost quality of municipal wastes or manure and is compared with cited results.

REFERENCES

- Y.K. Jeong and J. S. Kim. "A new method for conservation of nitrogen in aerobic composting processes". Bioresour. Technology, no. 79, pp. 129-133. 2001.
- [2] M.S. Switzenbaum, C. Holden, H. Soares and G. A. Kuter. "Effect of amendments on nitrogen conservation in wastewater biosolid composting". Compost Sci. Utilization, vol. 2, no. 2, pp. 35-42, 1994.
- [3] N. Morisaki, C. G. Phae, K. Nakasaki, M. Shoda and H. Kubota. "Nitrogen transformation during thermophilic composting". J. Ferment. Bioeng., no. 67, pp. 57-61, 1989.
- [4] Y. Eklind, and H. Kirchmann. "Composting and storage of organic household waste with different litter amendments". II. Nitrogen turnover and losses. Bioresour. Technol., vol. 74, no. 2, pp. 125-133, 2000.
- [5] E. Witter, and J. Lopez-Real., "Nitrogen losses during the composting of sewage sludge, and the effectiveness of clay soil, zeolite, and compost in adsorbing the volatilized ammonia". Biol. Wastes, vol. 23, no. 4, pp. 279-294. 1988.
- [6] R.C. Hansen, H.M. Keener, H.A.J. Hoitink. "Poultry manure composting: Design guidelines for ammonia". ASAE paper, No. 89-4075. ASAE, St. Joseph, MI. 10p. 1989.
- [7] M.T. Baca, F. Fornasier, M. De Nobili. "Mineralization and humification pathways in two composting process applied to cotton wastes". J. Ferment. Bioeng. vol. 74, no. 3, pp. 179–184, 1992.
- [8] N. Brink, "Composting of food waste with straw and other carbon sources for nitrogen catching". Acta. Agric. Scandinavica-Section B Soil Plant Sci. vol. 45, pp. 118–123, 1995.
- [9] S. Mahimairaja, N.S. Bolan, M.J. Hedley, A.N. "Macgregor. Losses and transformation of nitrogen during composting of poultry manure with different amendments: an incubation experiment". Bioresour. Technol. Vol. 47, no. 3, pp. 265–273, 1994.
- [10] Y. Liang, J. J. Leonard, J. J. R. Feddes and W. B. McGill. "Influence of carbon and buffer amendment on ammonia volatilization in composting". Bioresour. Technol., vol. 97, pp. 748-761. 2006.
- [11] S. Subair, J. W. Fyles and I. P. O,Halloran. "Ammonia volatilization from liquid hog manure amended with paper products in the laboratory". J. Environ. Qual. Vol. 28, pp. 202-207. 1999.
 [12] M. Meyer, and H. Sticher. "The significance of straw content for the
- [12] M. Meyer, and H. Sticher. "The significance of straw content for the retention of nitrogen during the composting of cattle manure". Z. Pflanzenernaehr. Bodenk no. 46, pp. 199–206. 1983.
- [13] R. Singh and Pradhan, K. "Determination of nitrogen and protein by Kjeldahl method. In: Forage Evaluation Science". Pvt. Publishers Ltd., New Delhi, p. 23. 1981.
- [14] J.A. Walkey and J.A. Black. "Estimation of organic carbon by the chromic acid titration method". Soil Sci. vol. 37, pp. 29-31. 1934
- [15] P.F. "Storm. Effect of temperature on bacterial species diversity in thermophilic solid-waste composting". Appl. Environ. Microbiol. Vol. 50, no. 4, pp. 899-905. 1985.
- [16] B. Xi, G. Zhang and H. Liu. "Process kinetics of inoculation composting of municipal solid waste". J. Hazard. Mat. B124, pp. 165-172. 2005.
- [17] J.R. Freney, J. R. Simpson and O. T. Denmead. "Volatilization of ammonia. In: Freney, J. R., J. R. Simpson (Eds.), Gaseous Loss of

Nitrogen from Plant-Soil Systems". Martinus Nijhoff/Dr. W. Junk

- Publishers, Hingham, MA, pp. 1-32. 1983. [18] K. Nakasaki, H. Yaguchi, Y. Sasaki and H. Kubota. "Effects of pH control on composting of garbage". Waste Manag. Res., vol. 11, pp. 117-125. 1993.
- [19] D.S. Carey, H. M. Keener and D. L. Elwell. "The effect of ammonium sulfate addition to partially to composted poultry manure". ASAE paper. No. 98-4099. St. Joseph, MI. 20p. 1998.
- [20] K. Ekinci, H. M. Keener and D. L. Elwell. "Composting short paper fiber with broiler litter and additives: I. Effect of initial pH and carbon/nitrogen ratio on ammonia emission". Composting Sci. Utiliz. Vol. 8, pp. 160-172. 2000.
- [21] M. Kithom, J. W. Paul and A. A. Bomke. "Reducing nitrogen losses during simulated composting of poultry manure using absorbents or chemical amendments". J. Environ. Qual. 28: 194-201.1999.
- [22] E. Witter and H. Kirchmann. "Effects of addition of calcium and magnesium salts on ammonia volatilization during manure composting". Plant and Soil, vol. 115, pp. 53-58. 1989.
- [23] K.N. Ohliger, T. M. Young and E. D. Schroeder. "Kinetics effects on preferential struvite accumulation in wastewater". J. Environ. Engineering ASCE, vol. 125, no. 8, pp. 730-737. 1999.