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Minimizing ammonia volatilization in waterlogged soils through mixing of urea with zeolite and sago waste water

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Loss of ammonia through volatilization is one of the major mechanisms which lead to poor urea-N use efficiency. In line with this, a laboratory study was carried out to determine the effect of mixing urea with zeolite and sago waste water on ammonia volatilization, soil exchangeable ammonium and available nitrate contents compared with urea without additives under waterlogged condition. The soil used in the experiment was Bekenu series (Fine loamy, siliceous, isohyperthermic, red-yellow to yellow Tipik Tualemkuts). This study was compared with five different mixture treatments which are: soil alone (T0), urea without additives (T1), urea mixed with 175 mL sago waste water and 0.75 g zeolite (T2), urea mixed with 175 mL sago waste water and 1.0 g zeolite (T3), and urea mixed with 175 mL sago waste water (T4). The mixtures (T2, T3 and T4) significantly minimized ammonia volatilization by between 40 and 50% compared with urea without additives (T1). These treatments (T2, T3 and T4) also significantly improved retention of soil exchangeable ammonium by 40 to 50% compared with urea without additives (T1). Additionally, the treatments significantly increased soil available nitrate nitrogen compared to urea without additives. Ammonia volatilization from urea could be significantly minimized under waterlogged condition, if urea is amended with sago waste and zeolite. Urea-N efficiency could be increased in waterlogged soils as the approach adopted in this study ensures effective retention of soil exchangeable ammonium and timely availability of soil nitrate nitrogen for plant use.

Key words: Ammonia volatilization, sago waste water, exchangeable ammonium, available nitrate nitrogen, nitrogen.

INTRODUCTION

During hydrolysis, urea N is converted into ammonia (NH_3) which subsequently reacts with a proton to produce NH_4^+. Under alkaline condition, the equilibrium of $NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$ shifts more to NH_3 thus increasing risk of volatilization losses that lead to lower fertilizer user efficiency (Sparks, 2005). As a result, ammonia volatilization is more serious if urea is surface applied and not incorporated into soils.

After surface application, urea is quickly hydrolyzed within 1 to 2 days by urease to NH_4^+, hydroxyl (OH^-) and carbonate (CO_3^{2-}) ions, leading to a high pH and very high concentrations of ammonium (NH_4^+) around the urea prill. This NH_4^+ reaches equilibrium with the dissolved NH_3 near soil surface. The sharp increase in soil pH (Zhengping et al., 1991) increases the likelihood of gaseous NH_3 losses to the atmosphere. This loss ranges between 1 to 60% of the applied N (Gioacchini et al., 2002).

To minimize the ammonia losses, zeolites can be used to minimize NH_3 volatilization because of their high CEC and great affinity for NH_4^+ (Stumpe, 1984; Mackdown and Tucker, 1985; Ming and Dixon, 1986). The importance of zeolite has been recognized by some studies because of their small internal channels which have been found to protect NH_4^+ from excessive nitrification by microbes

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(Ferguson and Pepper, 1987).

Acid source such as sago waste water may help to reduce NH₃ loss. Malaysia as the principal producer of sago (*Metroxylon sagu*), exports approximately 25,000 to 40,000 tonnes of sago starch annually (Apun et al., 2009). Most of these wastes are likely to be disposed into rivers because the factories operate near rivers. This practice may in the end contribute to water pollution. Considering the acidic nature of sago waste water (pH 3.5), the water could be put to good use by using it to decrease NH_3 loss from urea, as ammonia volatilization in flooded or waterlogged soils is largely controlled by pH and ammonium ions. Amending urea with peat water, sago waste water and zeolite may help in controlling soil pH through inhibition of ureolytic activity of micro organisms and the properties of zeolite may contribute to decrease NH_3 volatilization by inhibiting nitrification. Therefore, this study was carried out to determine the effect of mixing urea with zeolite and sago waste water on ammonia volatilization, soil exchangeable ammonium and available nitrate contents, compared with applied urea without additives under waterlogged condition.

MATERIALS AND METHODS

The clinoptilolite zeolite used in this study was imported from Indonesia. Sago palm (*M. sagu*) waste water was collected from Song Ngeng Sago Industries, Dalat, Mukah, Sarawak, Malaysia. The mineral soil used in this study was taken from an undisturbed area of Universiti Putra Malaysia, Bintulu Sarawak Campus, Malaysia using an auger. The soil taken at 0 – 15 cm depth was air dried and ground to pass 2.0 mm sieve for laboratory experiment. The soil texture was determined using the hydrometer method (Tan, 2005) and its field capacity and bulk density were determined by the method described by Tan (2005). The pH of the soil and zeolite were determined in a ratio of 1:2 (soil: distilled) water suspension and 1M KCl solution using a glass electrode (Peech, 1965). However, the pH of the sago waste water was determined directly from filtered samples using a glass electrode. The soil total carbon was determined using the loss-on-ignition method (Piccolo, 1996). Soil available P was extracted using the double acid method (Tan, 2005) followed by blue method (Murphy and Riley, 1962). The Kjedhal method was used to determine total N (Bremner, 1965). Exchangeable cations were extracted using the leaching method (Cottenie, 1980) and their concentrations were afterwards determined using followed Atomic Absorption Spectrometry (AAS). Soil CEC was determined by the leaching method followed by steam distillation (Bremner, 1965). The CEC of clinoptilolite zeolite was determined using the CsCl method (Ming and Dixon, 1986). It must be noted that the CsCl method used is the most suitable method because the leaching method tends to under estimate CEC of zeolites because of trapping of ammonium ions in the zeolites channels.

The treatments evaluated per 250 g soil were:

(1) Soil only (T0)
(2) 2.02 g urea (T1)
(3) 2.02 g urea + 0.75 g zeolite + 175 mL sago waste water (T2)
(4) 2.02 g urea + 1.00 g zeolite + 175 mL sago waste water (T3)
(5) 2.02 g urea + 175 mL sago waste water (T4).

These materials were mixed thoroughly to get homogenous mixture. The 250 g soil samples in 500 mL volumetric flask were moistened with distilled water at 70% field capacity. To achieve waterlogged condition, the treatments were used to saturate the soil samples in the 500 mL volumetric flasks after which they were sealed with parafilm and kept closed throughout the entire experiment.

The daily loss of NH_3 from urea was measured by using a closed-dynamic air flow system method (Siva et al., 1999; Ahmed et al., 2006a, 2006b). The system consisted of an exchange chamber of 500 mL conical flask containing 250 g soil sample and 250 mL conical flask containing 75 mL of boric acid which were both stop and fit with an inlet/outlet. The inlet of the chamber was connected to an air pump and the outlet was connected by silicon tubing which contained boric acid and indicator solution to trap ammonia gas (Ahmed et al., 2006a, 2006b). Air was passed through the chamber at the rate of 3.5 /L/min/chamber. This air flow rate was set and maintained throughout the incubation period using a Gilmont flow meter (Gilmont Instrument, Great Neck, New York).

The released NH_3 (g) captured in a trapping solution which contained 75 mL of boric acid with bromocresol green and methyl red indicators was titrated with 0.1 M HCl to estimate the amount of NH_3 (g) released. The entire incubation was conducted at room temperature. The boric acid indicator which was used to capture NH_3 (g) was replaced every 24 h during incubation for 13 days; a period when ammonia loss was less than 1% (Ahmed et al., 2006a, 2006b). After 13 days of incubation, soil samples were analyzed for pH, exchangeable NH_4^+ and available NO_3^- nitrogen. Soil pH was determined by the method previously stated. The method of Keeney and Nelson (1982) was used to extract soil exchangeable NH_4^+ and available NO_3^- followed by steam distillation. The experimental design was a completely randomized design with three replicates for each treatment. Analysis of variance was used to test mixture treatment effects and means of treatments were compared using Tukey's test (SAS version 9.2).

RESULTS AND DISCUSSION

The selected physical and chemical properties of Bekenu series are summarized in Table 1. The texture of the soil was sandy clay loam with a bulk density of 1.51 g cm⁻³. The soil was acidic, and it had 0.15% N, 0.57% organic carbon, and 2.28% organic matter. The soil exchangeable Ca, Mg and K contents were 2.05, 0.18 and 0.16 mg kg⁻¹, respectively. Available soil P was 2.39 mg kg⁻¹. The soil CEC was 7.33 cmol kg⁻¹. The aforementioned chemical properties were consistent with those reported by Paramananthan (2000) except for exchangeable Ca, which was relatively high probably because of liming (Table 1).

As expected, the pH of the sago waste water and zeolite were acidic while the pH of urea was basic (Table 2). The CEC of zeolite was high as well as its exchangeable Ca, Mg and K contents.

The daily NH_3 loss is demonstrated in Figure 1. As can be seen in Figure 1, soil alone did not contribute to ammonia loss throughout the incubation period. The ammonia loss started a day after the treatments were applied except for T2, T3 and T4; which significantly delayed ammonia loss for 6, 4 and 3 days respectively. These three treatments were urea amended with zeolite and sago waste water (Figure 1).

The total amount of ammonia lost at 13 days of

**Table 1.** Selected physico-chemical properties of Bekenu series.

Property	Value obtained	Standard data range*
pH (water)	4.11	4.6 – 4.9
pH (1.0M KCl)	3.86	3.8 – 4.0
CEC (cmol kg^{-1})	7.33	3.86 – 8.46
Texture	SCL	SCL
Bulk density (g cm^{-3})	1.51	nd
Organic matter (%)	2.28	nd
Available P (mg kg^{-1})	2.39	nd
Total nitrogen (%)	0.15	0.04 – 0.17
Organic carbon (%)	0.57	0.57 – 2.51
Exchangeable Ca (mg kg^{-1})	2.05	0.05 – 0.19
Exchangeable Mg (mg kg^{-1})	0.18	0.07 – 0.21
Exchangeable K (mg kg^{-1}) 0.16	0.16	0.05 – 0.19

Cation exchange capacity (CEC); sandy clay loam (SCL); not determined (nd); * means: Standard data range (Paramananthan, 2000).

Table 2. Selected chemical properties of zeolite, sago waste water and urea.

Property	Zeolite	Sago waste water	Urea
pH (water)	6.52	3.87	8.00
pH (1.0M KCl)	5.38	nd	nd
CEC (cmol kg^{-1})	100.33	nd	nd
Total Nitrogen (%)	nd	0.18	nd
Exchangeable Ca (mg kg^{-1})	20.19	0.21	nd
Exchangeable Mg (mg kg^{-1})	31.50	0.17	nd
Exchangeable K (mg kg^{-1})	28.16	0.19	nd

Cation exchange capacity (CEC); not determined (nd).
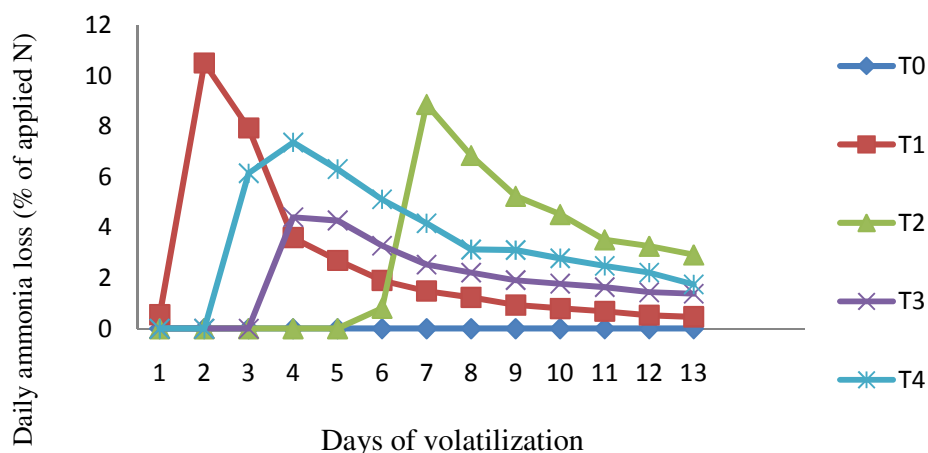
Figure 1. Ammonia volatilization over 13 days of incubation under waterlogged condition.

incubation is presented in Table 3. All the treatments with zeolite and sago waste water (T2, T3 and T4) significantly decreased ammonia loss compared to urea without additives (T1) with the larger amount of zeolite having the greatest effect. The ability of the mixtures tested to significantly minimize ammonia loss was partly because the sago waste water may have temporary acidified the soil surrounding urea-zeolite-sago waste water mixture because, when the soil pH is less than 5.5, urea hydrolyzes slowly (Fan and Mackenzie, 1993). As a

Table 3. Daily ammonia loss and soil pH from incubation under waterlogged condition.

Treatment	Ammonia loss (%)	Soil pH (water)
T0	0[d]	5.40[c]
T1	42.87[a]	7.21[a]
T2	26.39[b]	6.95[b]
T3	19.85[c]	7.03[ab]
T4	25.28[b]	7.09[ab]

Means with the same letter are not significantly different by Duncan's test at p ≤ 0.05.

Table 4. Accumulation of exchangeable ammonium and available nitrate at 15 days of incubation.

Treatment	NH_4^-N (ppm)	NO_3^- N (ppm)
T0	12.07[d]	1.55[d]
T1	78.09[c]	22.80[c]
T2	177.87[a]	34.00[ab]
T3	166.50[ab]	38.76[a]
T4	126.78[b]	24.76[bc]

Means with the same letter are not significantly different by Duncan's test at p ≤ 0.05.

result, this process effectively increased the volume soil with which urea mixes, and also increased the time required for complete hydrolysis (Fan and Mackenzie, 1993). Upon urea hydrolysis, lower soil pH facilitated formation of ammonium ions over ammonia, hence the decrease in ammonia loss in this study. In a related study, Rosliza et al. (2009) attributed increased formation of ammonium ions over ammonia to lower soil pH upon amending urea with humic and fulvic acids. The authors reasoned that lower soil pH retarded urea hydrolysis. Other studies which used humic and fulvic acids, isolated from various sources such as coal, peat and palm oil mill effluent sludge to amend urea associated ammonia loss to adsorption of ammonium ions at the exchange sites of the function groups such as carboxylic-COOH and phenolic-OH of these acids (Ameera et al., 2009; Regis et al., 2009; Susilawati et al., 2009; Rosliza et al., 2009a, 2009b) (Table 3).

There was a significant accumulation of soil exchangeable ammonium and available nitrate nitrogen with all the mixtures compared to urea without additives (Table 4). This finding was consistent with those of Rosliza et al. (2009a, 2009b) and Fan and Mackenzie (1993). The higher content of ammonium ions in this study suggests that the inclusion of zeolite has improved the soil to retain ammonium as well as minimizing the conversion of ammonium to nitrate. At 13 days of incubation, only the soil pH of T2 among the mixtures was significantly different compared with T1 (urea alone), and this was because the ammonia loss at this period did not vary significantly, that is about 1% of the N added as urea (Figure 1 and Table 4).

The high retention of ammonium ions observed in this study could be associated with the high CEC (100.33 cmol/kg) of the zeolite in T2, T3 and T4. This is because, the channels in zeolites effectively absorb ammonium ions and release them slowly. A study has shown that ammonium-exchanged clinoptilolite zeolite acted as a slow-release fertilizer in a medium textured and porous soil (Lewis et al, 1984). The authors also showed that clinoptilolite zeolite reduced ammonia volatilization when urea and clinoptilolite were applied to a coarse-textured alkaline soil. In this regard, the high loss of ammonia from urea without additives was possible because of the increased alkalinity from urea hydrolysis exceeding the localized buffer capacity of the soil or its ammonium retention ability.

Conclusion

The results of this study suggest that mixing urea with zeolite and sago waste water has great advantage over urea without additives. The mixture increases the formation of ammonium and available nitrate ions over ammonia, as well as retaining ammonium and nitrate nitrogen within the soil.

REFERENCES

Ahmed OH, Aminuddin H, Husni MHA (2006a). Effect of urea, humic acid, and phosphate interactions in fertilizer microsites on ammonia volatilization, soil ammonium and nitrate contents. Int. J. Agric. Res., 1: 25-31.
Ahmed OH, Aminuddin H, Husni MHA (2006b). Reducing ammonia loss from urea and improving soil-exchangeable ammonium retention through mixing triple superphosphate, humic acid and zeolite. Soil Use Manage., 22: 315-319.
Ameera AR, Ahmed OH, Nik Muhamad AM, Jalloh MB (2009). Reducing ammonia loss from urea by mixing with humic and fulvic acids isolated from coal. Am. J. Environ. Sci., 5(3): 420-426.
Apun K, Lihan S, Wong MK, Bilung LM (2009). Microbiological characteristics of trunking and non-trunking sago palm peat soil. Programme and abstract. 1st ASEAN sago symposium 2009. Current trend and development in sago research. October 29-30, 2009. Riverside Majestic Hotel, Kuching, Sarawak, Malaysia.
Bremner JM (1965). Total Nitrogen. In, Method of soil analysis, Part 2, Black CA, Evants DD, Ensminger LE, White JL, Clark FE, Dinauer RC (eds.), Am. Soc. Agron. Madison, Wisconcin, pp. 1149-1178.
Cottenie A (1980). Soil testing and plant testing as a basis of fertilizer recommendation. FAO Soils Bull., 38: 70-73.
Fan MX, Mackenzie AF (1993). Urea and phosphate interactions in fertilizer microsites: ammonia volatilization and pH changes. Soil Sci. Soc. Am. J., 57: 839-845.
Ferguson GA, Pepper IL (1987). Ammonia retention in sand amended

with clinoptilolite. Soil Sci. Soc. Am. J., 51: 231-234.

Gioacchini P, Nastri A, Marzadori C (2002). Influence of urease and nitrification inhibitors on N losses from soils fertilized with urea. Biol. Fert. Soils, 36: 129-135.

Keeney DR, Nelson DW (1982). Nitrogen-inorganic forms. In, Method of Soil Analysis, Part 2 (2nd ed), Page AL, Keeney DR, Baker DE, Miller RH, Ellis R, Rhoades JD(eds.). Agronomy Monograph, 9. ASA and SSSA, Madison, Wisconsin.

Lewis MD, Moore FD III, Goldsberry KL (1984). Ammonium-exchange clinoptilolite and granulated clinoptilolite with urea as nitrogen fertilizers. In, Zeo-agriculture: use natural zeolites in agriculture and aquaculture, Pond WG, Mumpton FA (eds.), Westview Press, Boulder, CO.

Mackdown CT, Tucker TC (1985). Ammonium nitrogen movement in a coarse-textured soil amended with zeolite. Soil Sci. Soc. Am. J., 49: 235-238.

Ming DW, Dixon JB (1986). Clinoptilolite in South Texas soils. Soil Sci. Soc. Am. J. 50: 1618-1622.

Murphy J, Riley JI (1962). A modified single solution method for the determination of phosphate in natural waters. Anal. Chem. Acta, 27: 31-36.

Paramananthan S (2000). Soils of Malaysia: Their characteristics and identification. (Volume 1). Academy of Science Malaysia, Kuala Lumpur, Malaysia.

Peech HM (1965). Hydrogen-ion activity. In, Method of soil analysis, part 2, Black CA, Evants DD, Ensminger LE, White JL, Clark FE, Dinauer RC(eds.), Am. Soc. Agron., Madison, Wisconsin, pp. 914-926.

Piccolo A (1996). Humus and soil conservation. Humic substances in terrestrial ecosystem. Piccolo A, (ed.) Elseiver, Amsterdam, pp. 225-264.

Regis B, Ahmed OH, Nik Muhamad AM (2009). Reduction of ammonia loss through mixing urea with humic acids isolated from peat soil (Saprists). Am. J. Environ. Sci., 5(3): 393-397.

Rosliza S, Ahmed OH, Nik Muhamad AM, Jalloh MB (2009a). Reduction of ammonia volatilization through mixing urea with humic and fulvic acids isolated from palm oil mill effluent (POME) sludge. Am. J. Environ. Sci., 5(3): 382-386.

Rosliza S, Ahmed OH, Nik Muhamad AM (2009b). Controlling ammonia volatilization and improving soil exchangeable ammonium and nitrate retention by mixing urea with humic acid, fulvic acid and triple superphosphate and muriate of potash. Am. J. Environ. Sci., 5(5): 605-609.

Siva KB, Aminuddin H, Husni MHA, Manas AR (1999). Ammonia volatilization from urea as affected by tropical-based palm oil effluent (pome) and peat. Commun. Soil Sci. Plant Anal., 30: 785-804.

Stumpe JM, Vlek PLG, Linday WL (1984). Ammonia volatilization from urea and urea phosphates in calcareous soils. Soil Sci. Soc. Am. J., 48: 921-926.

Susilawati K, Ahmed OH, Nik Muhamad, AM, Khanif Y (2009). Reduction of ammonia loss by mixing urea with liquid humic and fulvic acids isolated from tropical peat soil. Am. J. Agric. Biol. Sci., 4(1): 18-23.

Tan KH (2005). Soil sampling, preparation, and analysis (2nd ed). Boca Raton, Florida, USA.

Zhengping W, Van Cleemput O, Liantie L, Baert L (1991). Effect urease inhibitors on urea hydrolysis and ammonia volatilization. Biol. Fert. Soils, 11: 43-47.