Full Length Research Paper

Reducing ammonia loss from urea and improving soil exchangeable ammonium and available nitrate in non waterlogged soils through mixing zeolite and sago (*Metroxylon sagu*) waste water

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Ammonia loss from urea significantly reduces urea-N use efficiency. The objective of this study was to determine the effect of mixing urea with zeolite and sago (*Metroxylon sagu*) waste water on ammonia volatilization, soil exchangeable ammonium and available nitrate compared with urea alone. The mixtures significantly reduced ammonia loss by 22 to 41% compared with urea alone (straight urea, 46% N). All the mixtures of zeolite and sago waste water with urea significantly increased soil exchangeable ammonium by (39 to 49 ppm) and available nitrate by (0.23 to 2.06 ppm). The mixtures also temporarily reduced soil pH. The temporary reduction of soil pH may have retarded urea hydrolysis. It could be possible to improve the efficiency of urea-N applied to high value crops by addition of zeolite and sago waste water.

Key words: Urea, ammonia loss, sago waste water, exchangeable ammonium, available nitrate.

INTRODUCTION

Urea hydrolysis leads to the conversion of urea-N to ammonia. Subsequently, the ammonia reacts with a proton to produce ammonium ions. This process normally leads to sharp increase in soil pH (beyond 7) and ammonium ions around the urea granule. In such an alkaline condition, more ammonia is produced and increasing volatilization losses means lower urea-N use efficiency (Howard and Tyler, 1989; Zhengping et al., 1991; Gioacchini et al., 2002).

In order to control ammonia volatilization, phosphoric acid and acidic phosphates have been used to control ammonia loss through reduction of microsite pH (Fan and Mackenzie, 1993; Fenn and Richards, 1989; Fenn et al., 1990). However, apart from the high cost of amending these acidic materials, when they are mixed urea, the end product is corrosive and such a product requires special precautions in handling and storage. Even if their use encourage formation of ammonium ions over ammonia gas, without good retention of the ammonium ions in the soil, efficient use of these ions by plants cannot be guaranteed as both ammonium and nitrate ions are subject to leaching (Brady and Weil, 2002). In addition, plant N can be decreased by the biological transformation of ammonium to nitrate under anaerobic conditions, and nitrate can also be biologically denitrified to gases which lead to additional loss of N from soil (Brady and Weil, 2002). In order to reduce ammonia loss and at the same time addressing the aforementioned problems associated with the use of inorganic acids which lack the ability to efficiently retain ammonium ions in the soil, sago waste water (for reducing microsite pH) and zeolite (for retention of ammomium ions) could be mixed with urea.

Zeolites can be used to reduce ammonia volatilization because of their high CEC and great affinity for

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ammonium ions (Stumpe et al., 1984; Mackdown and Tucker, 1985; Ming and Dixon, 1986). Zeolites play a major role in controlling ammonia volatilization because of their small internal channels which have been found to protect ammonium ions from excessive nitrification by microbes (Ferguson and Pepper, 1987). An acidic source such as sago waste water may also help to reduce ammonia loss via reduction of soil pH. Malaysia as one of the major producers of sago (*Metroxylon sagu*), exports approximately 25,000 to 40,000 tonnes of sago starch annually (Apun et al., 2009). As a result, Malaysia produces substantial waste products in both solid and liquid forms which are likely to be disposed into rivers because sago factories operate near rivers.

This practice may in the end contribute to water pollution. Considering the acidic nature of sago waste water, the water could be put to good use through reduction of ammonia loss from urea. Amending urea with sago waste water and zeolite may control soil pH through inhibition of ureolytic activity of microorganisms while the aforementioned properties of zeolite may contribute to reduction of ammonia volatilization by encouraging formation of ammonium and nitrate ions over ammonia. Therefore, the objective of this study was to determine the effect of mixing urea with zeolite and sago waste water on ammonia volatilization, soil exchangeable ammonium and available nitrate, compared with urea alone under non 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 (Bekenu Series; fine loamy, siliceous, isohyperthermic, red-yellow to yellow Tipik Tualemkuts) used in this study was sampled in an undisturbed area of University Putra Malaysia Bintulu Sarawak Campus, Malaysia using an auger. The soil taken at 0 to 15 cm depth was air dried and ground to pass 2.0 mm sieve for the laboratory experiment. The soil texture was determined using the hydrometer method (Tan, 2005) and its field capacity and bulk density determined using the method described by Tan (2005). The pH of the soil and zeolite were determined in a 1:2 soil: distilled water suspension and KCl using a glass electrode (Peech, 1965). 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 then determined using 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 underestimate 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 obtain homogenous mixtures. The 250 g soil samples in 500 ml volumetric flask were moistened with distilled water at 70% field capacity. The daily loss of ammonia 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 stoppered and fit with an inlet/outlet. The inlet of the chamber was connected to an air pump and the outlet was connected by polyethylene tubing which contains 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 rate of air flow was maintained throughout the incubation period using a Gilmont flow meter (Gilmont Instrument, Great Neck, New York) to measure and adjust the air flow when necessary.

The released ammonia trapped in a solution which contains 75 ml of boric acid with bromocresol green and methyl red indicator was titrated with 0.1 M HCl to estimate the amount of ammonia released. The entire incubation was conducted at room temperature. The boric acid indicator which was used to capture ammonia 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 ammonium and available nitrate. Soil pH was determined by the method previously stated. The method of Keeney and Nelson (1982) was used to extract soil exchangeable ammnonium and available nitrate 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 treatment effects and means of treatments were compared using Duncan's test (SAS version 9.2).

RESULTS AND DISCUSSION

The selected physical and chemical properties of Bekenu series are summarized in Table 1. The aforementioned properties were comparable with those reported by Paramananthan (2000) except for exchangeable Ca, which was relatively high probably because of liming. 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 ammonia loss is summarized in Figure 1. Soil alone did not contribute to ammonia loss throughout the incubation period (Figure 1). The ammonia loss started a day after the treatments but the loss with urea alone (T_1) was higher than those of the mixtures (T_2, T_3, and T_4) containing urea amended with zeolite and sago waste water (Figure 1).

Over the period of incubation (13 days), the total amount of ammonia loss for all the treatments with zeolite and sago waste water (T_2, T_3, and T_4) were significantly lower compared with urea alone (T_1) (Table 3). These mixtures also temporary reduced the soil pH compared with urea alone (Table 3). The mixtures (T_2, T_3, and T_4) tested significantly reduced ammonia loss partly because

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

Property	Value obtained	Standard data range*
pH (water)	4.11	4.6 – 4.9
pH (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)	2.39	nd
Total Nitrogen (%)	0.15	0.04 – 0.17
Organic carbon (%)	0.57	0.57 – 2.51
Exchangeable Ca (mg/kg)	2.05	0.05 – 0.19
Exchangeable Mg (mg/kg)	0.18	0.07 – 0.21
Exchangeable K (mg/kg)	0.16	0.05 – 0.19

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

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

Property	Zeolite	Sago waste water	Urea
pHw	6.52	3.87	8.00
pH (KCl)	5.38	nd	nd
CEC (cmol/kg)	100.33	nd	nd
Total Nitrogen (%)	nd	0.18	nd
Exchangeable Ca (mg/kg)	20.19	0.21	nd
Exchangeable Mg (mg/kg)	31.50	0.17	nd
Exchangeable K (mg/kg)	28.16	0.19	nd

CEC, cation exchange capacity; nd, not determined.
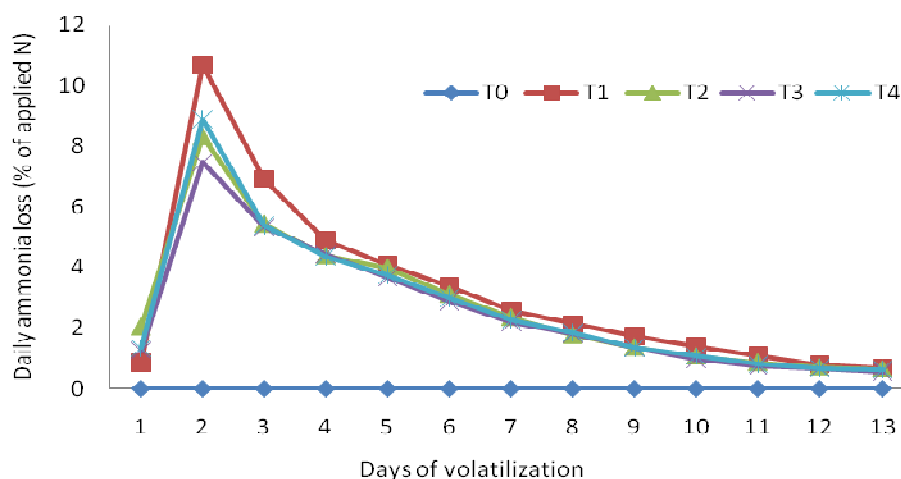
Figure 1. Daily loss of ammonia for 13 days of incubation in non waterlogged condition.

the sago waste water may have temporarily 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). This process may have effectively increased the volume of soil with which urea mixes, and also increased the time

Table 3. Total amounts of ammonia loss and soil pH over 13 days of incubation under non waterlogged condition.

Treatment	Ammonia loss (%)	Soil pH(water)
T0	0[e]	5.14[d]
T1	41.50[a]	7.68[a]
T2	32.37[c]	7.20[bc]
T3	24.38[d]	7.13[c]
T4	34.76[b]	7.40[b]

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

Table 4. Exchangeable ammonium and available nitrate at 13 days of incubation under non waterlogged condition.

Treatment	NH4-N (ppm)	NO3- N (ppm)
T0	11.98[d]	2.46[d]
T1	85.80[c]	4.30[c]
T2	131.35[a]	4.53[bc]
T3	134.85[a]	6.36[a]
T4	124.76[b]	4.76[b]

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

required for complete hydrolysis (Fan and Mackenzie, 1993). Upon urea hydrolysis, lower soil pH might have also improved formation of ammonium ions and available nitrate over ammonia (Table 4), hence the reduction in ammonia loss observed in this study.

There was significant accumulation of soil exchangeable ammonium and available nitrate with all the mixtures compared with urea alone (Table 4). This observation was comparable with that of Fan and Mackenzie (1993). The high content of ammonium ions in this study suggests that the inclusion of zeolite improved the soil ammonium retention as well as minimizing its conversion to nitrate. At 13 days of incubation, the soil pH of all the mixtures (T_2, T_3 and T_4) were significantly lower compared with urea alone (T_1), suggesting that the inclusion of sago waste water in particular temporary retarded urea hydrolysis.

The high retention of ammonium observed could also be linked to the high CEC (100.33 cmol/kg) of the zeolite in the mixtures (T_2, T_3, and T_4) as the channels in zeolites might have effectively absorbed ammonium ions and released them slowly. A study has shown that ammonium-exchanged clinoptilolite zeolite acted as a slow-release fertilizer in a medium textured, porous soil (Lewis et al., 1984). They also reported that clinoptilolite zeolite reduced ammonia volatilization when urea and clinoptilolite were applied to a coarse-textured alkaline soil. In relation to this review, the high loss of ammonia from urea alone (T_1) was possible because of the increased alkalinity from urea hydrolysis exceeding the localized buffer capacity of the soil or its ammonium retention ability.

Conclusion

Mixing urea with zeolite and sago waste water has great advantage over urea alone as the mixture encourages the formation of ammonium and available nitrate ions over ammonia. The mixture also improves retention of exchangeable ammonium and available nitrate within the soil.

ACKNOWLEDGEMENT

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