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Enhancing nitrogen availability from urea using clinoptilolite zeolite

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ABSTRACT

The high costs of nitrogen fertilizers have necessitated best-developed practices to optimize nitrogen fertilizers use whilst minimizing nitrate losses. Ammonium adsorption inhibits loss of nitrogen in the form of nitrate thereby increasing nitrogen availability for crops. Due to the negatively charged properties of nitrate, it moves freely in the soil solution and not adsorbed onto soil particle surfaces. In this study, clinoptilolite zeolite was used in soil leaching and ammonium adsorption and desorption studies to determine: (i) soil total nitrogen availability, exchangeable ammonium, and available nitrate, and (ii) the capacity of clinoptilolite zeolite to adsorb and desorb ammonium from different rates of urea. Different rates of urea amended with clinoptilolite zeolite significantly reduced ammonium and nitrate release from urea compared with urea alone. Clinoptilolite zeolite enhanced retention of soil total nitrogen, exchangeable ammonium, and available nitrate due to the high cation exchange capacity of the mineral to adsorb ammonium, thus, improving nitrogen availability through temporary retention on the exchange sites of the clinoptilolite zeolite. The availability of nitrogen can be enhanced if urea is amended with clinoptilolite zeolite.

1. Introduction

Plant available nitrogen (N) is positively influenced by N fertilization, mineralization of soil organic matter, and biological N fixation whereas nitrate (NO_3^-) leaching, immobilization, crop uptake and removal, denitrification, volatilization, soil run-off, and erosion have negative effects on N availability (Hofman and Van Cleemput, 2004). The relative importance of these processes depends on soil pH, topsoil texture, aeration, water supply and temperature, type, amount, placement and timing of N fertilizers, available carbon, crop residue management, tillage, soil compaction, and irrigation (Di and Cameron, 2002). The increased cost of N fertilizers and concerns about the adverse environmental impacts of N losses had prompted great interest in fine-tuning N fertilizer management. The need for the efficient management of N fertilizers is to match application source, rate, timing, and method to supply on-farm sources of N (*e.g.* chemical fertilizers or organic amendments) to meet crop requirement.

Ammonium (NH_4^+) adsorption is the process by which NH_4^+ is attached to the negative charged surfaces of mineral such as clinoptilolite zeolite (Daković et al., 2007). Ammonium adsorption is a beneficial process that improves N availability because the NH_4^+ remain available to crops besides being protected from losses due to leaching, runoff, and volatilization (Hatfield and Prueger, 2004). Desorption is the opposite of adsorption and it occurs when adsorbed nutrients are released from the surfaces of for example, soil organic matter or inorganic minerals such as clinoptilolite zeolite (Ashman and Puri, 2002).

Because of the size of NH_4^+, it is able to penetrate the internal spaces that lie between individual 2:1 clay minerals in minerals such as vermiculite, illite, and some forms of montmorillonite. Once held within the clay structure, NH_4^+ becomes available to crops. Both 2:1 and 1:1 clay minerals are made up of layers of silica and aluminium hydroxide. The silica layer consists of a series of silicon and oxygen atoms, in the ratio of 1:4, forming small pyramid-shaped structures known as silica tetrahedral (Ashman and Puri, 2002). In contrast to NH_4^+, NO_3^- is a negatively-charged anion, thus it is repelled by negatively charged soil colloids. Nitrate salts are highly soluble, move with soil water, and easily leached through soils (Brady and Weil, 2010). Leaching of NO_3^- represents a loss of crop available N from soils. According to Di and Cameron (2002), the two fundamental factors which determine the amount of NO_3^- leached from soils to groundwater are the amounts required by crop uptake and drainage volume. High NO_3^- leaching loss occurs when there is high amount of NO_3^- in soils' profile in conjunction with or followed by a high drainage volume

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(Di and Cameron, 2002).

Inhibiting the conversion of NH_4^+ to NO_3^- could minimize N loss. However, it is not possible to completely prevent the movement of some NO_3^- to water supplies, but good management practices can keep losses within acceptable limits (Lamb et al., 2014). Highly weathered soils have low N holding capacities because most or all of the minerals with significant negative charges are lost through weathering. Due to low N retention capacity and high permeability of these soils, heavy rainfall causes rapid NO_3^- leaching from N fertilizers (Renck and Lehmann, 2004). The use of clinoptilolite zeolite in agriculture has shown that both soil and plant can benefit from clinoptilolite zeolite additions (Ahmed et al., 2009; Latifah et al., 2017) because of the high ion-exchange and large adsorptive affinity of this mineral for water and NH_4^+ (Polat et al., 2004).

Zeolites are a group of highly crystalline hydrated aluminosilicates minerals, which when dehydrated, develop a porous structure with minimum pore diameters of between 0.3 and 1 nm. All zeolites are considered molecular sieve materials that can selectively absorb molecules based on their sizes (Peres-Caballero et al., 2008). This characteristic enables zeolite to retain cations such as NH_4^+ (Inglezakis et al., 2002). Gradual desorption of adsorbed NH_4^+ on the surface zeolites ensures slow-release N fertilizers for optimum plant uptake (Gruener et al., 2003; McGilloway et al., 2003; Rehakova et al., 2004).

For NH_4^+ removal from water and wastes, ion exchange using zeolites was reported to be the most effective and low-cost material (Sprynskyy, 2009). Ammonium ions are removed from aqueous solutions using zeolites by exchanging with cations or by adsorption in pores of aluminosilicate groups. Based on this rationale, it was hypothesized that the use of clinoptilolite zeolite could enhance N availability through NH_4^+ retention following application of urea. In this study, an attempt was made to optimize the use of urea by reducing urea by 25% and 50% of the standard recommended urea for *Zea mays* L. To this end, soil leaching and NH_4^+ adsorption and desorption studies were carried out to determine the: (i) availability of soil total N, exchangeable NH_4^+, and available NO_3^-, and (ii) capacity of clinoptilolite zeolite to adsorb and desorb NH_4^+ from different rates of urea.

2. Material and methods

2.1. Characterization of soil selected physical and chemical properties

The soil used in this study was Ultisols, *Typic Paleudults* (Bekenu Series). This soil is fine loamy, siliceous, isohyperthermic, red-yellow to yellow. It has an argillic horizon with fine sandy clay loam textures. The structure is generally weak medium to coarse sub angular blocky. It is friable in nature (Paramananthan, 2000). It was collected at 0–20 cm depth from an uncultivated area at Universiti Putra Malaysia Bintulu Campus Sarawak, Malaysia. The soil was air dried and ground to pass a 2 mm sieve for initial characterization. Soil texture and bulk density were determined using the method described by Tan (2005). Soil CEC was determined using the leaching method (Tan, 2005) followed by steam distillation (Bremner, 1965).

Soil pH was determined in a ratio of 1:2 (soil: distilled water suspension) using a pH meter. Total C, N, and organic matter of the soil were determined using Leco CHNS Analyzer (LECO Truspec Micro Elemental Analyzer CHNS, New York). The method of Keeney and Nelson (1982) was used to extract exchangeable NH_4^+ and available NO_3^- after which their contents were determined using steam distillation. Soil available P was extracted using the double acid method (Tan, 2005) followed by the molybdenum blue method (Murphy and Riley, 1962). Exchangeable cations were extracted using the leaching method (Tan, 2005) after which their contents were determined using Atomic Absorption Spectrophotometry (Analyst 800, Perkin Elmer, Norwalk, USA). The texture of the soil was sandy loam with a bulk density of 1.51 g cm^{-3}. These physical properties are consistent with those reported in Soil Survey Staff (2014). The selected chemical properties of the soil are summarized in Table 1. The soil pH, total N, and total C are also consistent with those reported by Paramananthan (2000) for Bekenu series whereas exchangeable Ca, Mg, and K are higher than the reported values of Paramananthan (2000).

Table 1
Selected chemical properties of Bekenu Series. S.E. is standard error. Standard data range reported by Paramananthan (2000). CEC is cation exchange capacity. nd is not determined.

Property	Value obtained Mean ± S.E	Standard data range
CEC (cmol$_c$ kg^{-1})	7.43 ± 0.15	8.0–24
pH$_{water}$	4.66 ± 0.10	4.6
Exchangeable calcium (cmol$_c$ kg^{-1})	1.41 ± 0.05	0.01
Exchangeable magnesium (cmol$_c$ kg^{-1})	1.53 ± 0.05	0.21
Exchangeable potassium (cmol$_c$ kg^{-1})	0.60 ± 0.02	0.19
Total nitrogen (%)	0.15 ± 0.01	0.04–0.17
Organic matter (%)	2.06 ± 0.10	nd
Total carbon (%)	1.20 ± 0.60	0.57–2.51
Available phosphorus (mg kg^{-1})	4.16 ± 0.13	nd
Exchangeable ammonium (mg kg^{-1})	19.85 ± 0.68	nd
Available nitrate (mg kg^{-1})	5.16 ± 0.09	nd

2.2. Chemical properties of clinoptilolite zeolite

The clinoptilolite zeolite used in this study was in powder form (sieved to pass 250 mm). Total N of the clinoptilolite zeolite was determined using Kjeldahl method (Bremner, 1965). The exchangeable NH_4^+ and available NO_3^- of the clinoptilolite zeolite were determined using the method described by Keeney and Nelson (1982). The pH of the clinoptilolite zeolite was determined in a ratio of 1:2 (clinoptilolite zeolite:distilled water suspension) using a pH meter. The CEC of the clinoptilolite zeolite was determined using the CsCl method (Ming and Dixon, 1986). This method was used to avoid underestimation of the CEC of the clinoptilolite zeolite as the CsCl method does not lead to entrapment of NH_4^+ in the channels of the clinoptilolite zeolite. The exchangeable K, Ca, and Mg of the clinoptilolite zeolite were extracted using the method of Ming and Dixon (1986). Thereafter, contents were determined using Atomic Absorption Spectrophotometry (Analyst 800, Perkin Elmer, Norwalk, USA).

The chemical properties of the clinoptilolite zeolite used in this study are summarized in Table 2. The CEC of the clinoptilolite zeolite was lower (100 cmol$_c$ kg^{-1}) than the value obtained from the supplier of clinoptilolite zeolite (160 cmol$_c$ kg^{-1}), however the value obtained in this study is within the standard range (Table 2). Ming and Dixon (1986) reported a range of clinoptilolite zeolite CEC as 100–300 cmol$_c$ kg^{-1}. This range depends on the amount of $A1^{3+}$ that replaces Si^{4+} in the clinoptilolite zeolite structure (Ming and Dixon, 1986). The pH, total N, Ca, Mg, and K of the clinoptilolite zeolite were lower than those obtained from the supplier of this mineral (Table 2).

Table 2
Selected chemical properties of clinoptilolite zeolite. S.E. is standard error. Data were obtained from Luxurious Empire Sdn. Bhd. Kulai Jaya, Malaysia.

Property	Present study (Mean ± S.E.)	Reference
pH	6.80 ± 0.03	8–9
CEC (cmol$_c$ kg^{-1})	100 ± 0.35	160
Total nitrogen (%)	1.18 ± 0.04	1.36
Calcium (mg kg^{-1})	18,400 ± 19.09	25,600
Magnesium (mg kg^{-1})	11,200 ± 4.48	15,000
Potassium (mg kg^{-1})	14,850 ± 10.17	22,600
Sodium (mg kg^{-1})	17,184 ± 5.43	17,600
Ammonium (mg kg^{-1})	12.60 ± 0.43	nd
Nitrate (mg kg^{-1})	11.58 ± 0.18	nd