



Evaluation of Zeolite Based Nitrogen Nano-fertilizers on Maize Growth, Yield and Quality on Inceptisols and Alfisols

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Authors' contributions

This work was carried out in collaboration between both authors. Author AM designed the study, performed and wrote the first draft of the manuscript with the guidance of author KSS. Both authors read and approved the final manuscript.

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ABSTRACT

Nano-fertilizer technology is designed to deliver nutrients in a regulated pattern in correspondence with the crop demand thereby nutrient use efficiency can be improved without associated ill-effects. This present study hypothesize that nano-zeolite possesses extensive surface area and its coating or blending with the conventional nitrogenous fertilizers can regulate the release of nitrogen. This serves as an excellent slow release fertilizer that assists in sustained release of nitrogen that commensurate with crop growth without associated environmental harm. The newly developed intercalated N nano-fertilizer formulations had been tested using maize as a model system. The fate of N in the soil system was examined in order to gain insights of nano-fertilizer in promoting productivity of crops with higher N use efficiency. Response of maize plants to the fabricated fertilizers were tested in two greenhouse experiments of two distinct soil textures (Inceptisol – Periyarayakkan palayam soil series – clay loam and Alfisols - Irugur soil series- sandy loam). The grain N content of nanozeourea on inceptisol (Control: 0.26%; Treated: 0.32%) and alfisols (Control 0.48; Treated 0.76%) were higher consistently. The response was more pronounced in alfisol than

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inceptisol. The growth, yield, quality and nutrient uptake were consistently higher for nanozeourea treatment than conventional urea.

Keywords: Alfisols; inceptisols; nano-fertilizer; nitrogen; maize yield; slow release; zeolite.

1. INTRODUCTION

Fertilizers are indispensable in agricultural production system. Application of fertilizers started in the country in 1960's which closely coincided with the introduction green revolution when fertilizer responsive varieties have been inducted in Indian agriculture. Despite fertilizer application remarkably increased the grain growth, the yields of several crops got plateaued due the low fertilizer response ratio, imbalanced fertilization, low organic matter, increased intensities of multi-micronutrient deficiencies across the country. Within the set of challenges faced by the soil scientists, imbalanced fertilization is one of the most critical factors to be considered for N management. Since N fertilization exhibits universal response in crops besides low price of urea due to decontrol (subsidized rate), farmers started using nitrogenous fertilizers particularly urea heavily which has led to the current NPK ratio of 8.2: 3.2: 1 while optimal ratio is stipulated as 4:2:1. This is very serious issue causing nitrate pollution in ground water and eutrophication in aquatic system. This necessitates to develop slow release fertilizers to regulate the nitrification processes thereby N availability be sustained during the crop period. Nanotechnology deals with manipulation of materials at atom level, molecular and macromolecular scales, which operate at 100 nm, their properties significantly, differed from at a large scale [1,2]. It increases surface area to volume ratio altering mechanical, thermal and catalytic properties of materials. Nanotechnology has potential to develop slow release efficient fertilizers [3]. As we are all aware that clays are the key factor in deciding the soil fertility due to the fact that the surface area is huge and it adsorptive sites assists in retention and release of nutrients.

One gram of montmorillonite can be spread to a dimension of 30-40 m² [4], if the same clay reduced by ball milling process and its dimension got reduced to nanometre that increase the surface area by several fold of 750 m² g⁻¹ [5]. Extensive studies have been done to exploit "top-down approach"

wherein the particles are subjected to intense grinding to reach the desirable size of 1-100 nm. In order to stabilize the particles, surfactants have been used. The surfactant had an added advantage of changing the surface charge of the particle which will allow the nano-particles to hold anionic nutrients (eg. NO₃⁻). This approach had been widely exploited to synthesize nano-fertilizers carrying nitrogen [6-10]. These nano-fertilizer formulations have a potential to increase nutrient use efficiencies under the greenhouse conditions [11]. Nano-fertilizers and nano composites can be used to control the release of nutrients [12] from the fertilizer granules so as to improve the nutrient use efficiency while preventing the fixation or loss of nutrients to the environment [13] and supply with range of nutrients in desirable proportions [14]. Zeolite and nanoporous zeolite used as a slow release fertilizer in farming [15,16]. Zeolite incorporated urea, potassium sulphate and calcium hydroxyapatite as a slow release nano-fertilizer increased availability for 60 days [17]. Synthesised clay polymer nutrient nanocomposite using crystalline and non-crystalline components of soil clays increased biomass yield [18]. Nanocomposite fabricated using nanoclays and zeolite for maize as a slow release fertilizer which regulated N availability up to 45-49 days [5]. Therefore, responses of maize plants to zeolite based nano N fertilizer formulations were undertaken on Inceptisols and Alfisols.

2. MATERIALS AND METHODS

Fine size natural zeolite (clintoptilolite) was procured from GM Chemicals, Allahabad. On the basis of zeolite forms (micro, nano) loading efficiency, the intercalation and impregnation of urea was done to produce novel nano-nitrogen fertilizer using both adsorbents [3]. Experiments were conducted in two types of soils (light and heavy textured i.e., Alfisols - Irugur soil series-sandy loam and Inceptisol – Periyayakkan palayam soil series – clay loam) to study the response of maize (NK-6240) to different fertilizer formulations during 2012 and 2013 at Tamil Nadu Agricultural University. Initial soil samples were analyzed for their physical and chemical properties (Table 1).

Table 1. Initial characteristics of the experimental soils

Properties	Inceptisols	Alfisols
	Coimbatore black soil	Bhavanisagar red soil
Clay (%)	42	15.6
Silt (%)	14.7	5.5
Fine sand (%)	16.2	46
Coarse sand (%)	21.6	31.8
Textural class	Clay loam	Sandy loam
pH (1:2.5)	8.52	8.4
EC (dSm ⁻¹)	0.2	0.06
CEC (cmol (p+) kg ⁻¹)	23.2	10.9
Bulk Density (gcm ⁻³)	1.44	1.62
Particle Density (gcm ⁻³)	2.65	2.61
Porespace (%)	52.3	32.1
Water holding capacity (%)	47.3	27.9
Total nitrogen (%)	0.09	0.03
Organic carbon (mg kg ⁻¹)	4200	3420
Available nitrogen (Kg ha ⁻¹)	154	148
Available phosphorus (Kg ha ⁻¹)	20	35
Available potassium (Kg ha ⁻¹)	638	907

The following 5 treatments were adopted in both soil conditions. The recommended dose of N for hybrid maize @ 250 kg N ha⁻¹ was followed for all the five treatments. The P & K were applied in the form of single super phosphate and murate of potash at the recommended dose of 75 and 75 kg P₂O₅ and K₂O, respectively.

- T1 Urea alone
- T2 Zeolite + Urea (1:1 ratio – Physical mixing at equal proportion on w/w basis)
- T3 Nano Zeolite + Urea (1:1 ratio - Physical mixing at equal proportion on w/w basis)
- T4 Zeourea (1:1) – Intercalated
- T5 Nanozeourea (1:1) – Intercalated

Plant height was measured at 30, 60, 90 and harvest stage. Total chlorophyll content in leaves was estimated by SPAD meter (Minolta SPAD52 meter) at 60 DAS [19] prior to emergence of tassel. Root length was determined by measuring the length of root from the base of the stem to the tip of the lengthiest root and expressed in cm. Dry matter production was estimated at post- harvest stage. The uptake of N was obtained by multiplying the dry matter with the nutrient content concentrations. The units expressed as g per pot.

2.1 Plant Nutrient Analysis

One g of digested samples were made up to 50 mL using distilled water and stored for further nutrients analysis. The nitrogen content of the plant samples were determined by the standard procedure. About 10 mL of the di acid digest was

taken and transferred to micro kjeldahl to distill the ammonia. 2% boric acid with 2-3 drops of double indicator was used to collect evolved ammonia and titrated against 0.02 N sulphuric acid. Blanks were maintained without adding sample. Crude protein was estimated by using the formula N (%) content × (6.25) conversion factor.

2.2 Yield Components

The number of days for the emergence of tassel and silking were recorded. The mean length of cob from bottom to the top was measured and expressed in cm. The mean girth of the cob at maximum girth was measured and expressed in cm. The mean number of grain rows cob⁻¹ was counted from the cob obtained from the sample plants and expressed. The total number of grains in each row of the cobs of sample plant was counted and mean was worked and expressed as number grains row⁻¹. The weight of individual cob was recorded after drying and the mean weight was arrived at and expressed in g cob⁻¹. The data collected from various experiments were subjected to analysis by variance (P = .05) with mean separation by least significant difference (LSD) as well as by DMRT [20].

3. RESULTS AND DISCUSSION

3.1 Plant Height (cm)

Maize plants fertilized with new fertilizer formulation derived from physical blending of

urea with zeolite or nano-zeolite or fusing through intercalation processes significantly increased the plant height especially at the active growth stage of the crop (60 & 90 DAS). Despite these new fertilizer formulations increased the growth but the level of significance was not observed during early stage and harvest. The treatment difference was quite obvious in plants fertilized with nanozeourea. The best treatment registered a plant height of 144.8 cm while conventional urea fertilization produced 131.8 cm at 90 DAS. Other treatments exhibited comparable plant heights. Similar trend of results were recorded in Alfisol with the exception that the values are higher by 15-20% in all the treatments (Table 2).

Plant height was considered as indicator of growth, differed with application of fertilizer source. Irrespective of soil, fertilizer application, the plant height increased over the vegetative growth period. This trend of growth and results are in corroboration with the findings of [21] sugarcane growth and yield significantly increased by the adding zeolite incorporated with chemical fertilizer and [22] zeolite application (@ 20 g and 40 g) had taken minimum days for emergence of unifoliate first, second, sixth trifoliate leaves and plant height of soyabean on

allophanic soil. The mixing of zeolite with wolverine sand improved the corn growth [23]. Consumption of 2 g zeolite in 1 kg soil had important effects on the leaf area and the diameter of maize, in comparison with control treatment it could effect on the yield [24]. The positive results obtained on maize plant height and grain yield on natural zeolite [25].

3.2 SPAD Value

The SPAD readings of urea-fertilized maize plants were compared with urea blended with zeolite or nano-zeolite. All plants had comparable in SPAD Meter readings and were statistically non-significant (Table 3).

SPAD meter reading on chlorophyll content at a tassel growth stage varied with amount of fabricated nitrogenous fertilizer fed and light intensity of maize micro climate of growth period. Chlorophyll content was determined with Minolta SPAD 52 meter of non-destructive method. Analogous findings observed strong correlation between dry matter yields with the amount of total N in tropical maize [26]. Similar readings recorded in [27] non-destructive chlorophyll meters have been used to predict N fertilizer requirement of maize.

Table 2. Effect of zeolite based N fertilizers on DAS of maize plant height (cm)

Treatments	Inceptisols				Alfisols			
	30	60	90	115	30	60	90	115
T ₁ - Urea	34.57	91.43	131.8	144.3	34.0	102.1	153.7	162.4
T ₂ - Zeolite +Urea	35.14	89.28	127.4	142.4	41.6	107.0	153.1	160.4
T ₃ - Nanozeolite + Urea	35.28	89.28	130.4	142.4	32.1	101.1	150.2	158.0
T ₄ - Zeourea	37.57	94.57	130.8	146.3	37.6	109.4	158.8	165.8
T ₅ -Nanozeourea	40.86	94.86	144.8	152.3	37.3	110.8	167.4	178.1
S.Ed	3.53	3.98	3.86	3.84	3.24	7.70	5.19	4.75
CD (0.05)	NS	NS	7.89	NS	NS	NS	NS	9.70

DAS- Days after sowing

Table 3. Effect zeolite based N fertilizers on maize SPAD Value, root length, Dry Matter Production (DMP), tasselling and silking

Treatments	SPAD value		Root length(cm)		DMP (g)		Tasseling (Days)		Silking (Days)	
	I	A	I	A	I	A	I	A	I	A
T ₁ - Urea	39.32	36.73	56.8	43.5	120.7	105.2	71.4	60.9	83.4	66.1
T ₂ - Zeolite +Urea	37.97	38.76	53.3	60.3	142.5	115.7	68.6	56.1	78.4	60.9
T ₃ -Nanozeolite+Urea	39.01	38.18	56.8	59.3	144.7	118.6	71.3	61.0	82.9	65.4
T ₄ - Zeourea	38.52	38.21	59.2	61.9	146.7	123.6	72.4	58.6	83.4	63.4
T ₅ -Nanozeourea	38.45	39.17	65.9	67.4	151.4	130.1	71.1	56.0	85.0	60.1
S.Ed	1.33	1.70	5.00	5.12	10.46	9.03	2.55	2.32	2.48	2.12
CD (.05)	NS	NS	NS	10.46	NS	NS	NS	NS	NS	4.34

I-Inceptisols, A-Alfisols

3.3 Root Length (cm)

Maize plants fertilized with either urea or new fertilizer formulations did not produce any statistical significance on root length in inceptisols (Table 3). However, nano-urea-fertilized plants had the highest values for root length and the value was 9.1% higher than control. On the other hand, in alfisol, nanozeourea fertilization increased the root length to the tune on 23.8% higher in comparison to urea-fertilized plants. The root length increase may be the effect of nanozeolite and as a consequence to physical contact of nanozeourea with root surface. Similar findings reported [28] that the highest increase of weight/length ratio of maize primary root was obtained for treatment with micronized clinoptilolite at the lowest dose of 0.1%, while a decrease was found for treatment with granular clinoptilolite, attesting the role of different clinoptilolite particles size on root development.

3.4 Total Dry Matter (g)

The dry matter production of maize plants did not differ significantly among the treatments especially at the harvest stage in both inceptisol and alfisol (Table 3). The highest dry matter yield obtained from nanozeourea treated soil may be attributed to the increased N availability due to reduced ammonia loss. Similar findings were recorded by [29] found that the activity of water after adding nano-materials was increased and N, P and K were absorbed into the plants with the absorbing of water, thus the dry matter production was also increased. Similar findings[30] revealed that the highest dry matter yield (29.25 g pot^{-1}) was obtained from gelatin + Cu coated urea and (26.50 g pot^{-1}) micronutrient coated urea treated pots, closely followed by (25.5 g pot^{-1}) Palm stearin + Cu coated urea, (26 g pot^{-1}), Agar + Cu coated urea and (20.75 g pot^{-1}) Cu coated urea. The uncoated urea produced the least dry matter yield (19 g pot^{-1}) at the same level of N application. Results indicated that N, P and K-enriched zeolite was an adequate slow-release nutrient source for plants. The enrichment of zeolite with chemical fertilizer (KNO_3 , K_2HPO_4 , H_3PO_4) improved the dry matter production and nutrient accumulation after successive crops of Lettuce, Tomato, Rice and Andropogon grass [31].

3.5 Days Taken for Tasseling and Silking

The number of days taken to tassel or silking did not differ significantly in an inceptisol. The

number of days to tassel was in the range of 68 to 72 days and silking in the range of 78-85 days. One of the striking response was in nanozeourea fertilized plants which took 85 days to silk which is 2 days longer than urea fertilized plants. In alfisol, the days to attain tasseling did not change significantly. But, there was a remarkable difference between red and black soils. Maize plants grown in alfisol had a early tasseling by 10-14 days in comparison to inceptisol. Such trend was also seen in silking. The conventional urea fertilized plants took 66 days while nanozeourea took 60.1 days and zeolite blended urea fertilized plants registered 60.9 days (Table 3).

3.6 Nitrogen Content (%)

In inceptisol, nitrogen contents of roots, shoots and grains were significantly influenced by fertilization with various forms of zeolite based N fertilizers. The highest N content was registered in roots of maize plants fertilized with nanozeourea (0.32%) while urea fertilized plants had only 0.26%. On the hand, zeourea fertilized plants had the highest N content of 0.78% which is significantly different from the rest of the treatments. Highest N content was registered in grains harvested from nanozeourea fertilized maize plants. Even in alfisol, N contents in maize plants were significantly different for various fertilizer formulations. Roots had the highest N uptake in zeourea or nanozeourea but they were significantly different from urea fertilized or physically blended urea with zeolite. Nitrogen contents in stover and grains were significantly higher in nanozeourea than other treatments. In grains, nanozeourea fertilized maize plants had 28% higher N content (0.76%) in comparison to urea fertilized plants (0.48%) (Table 4).

Nanozeourea fertilizer application caused a highly significant increase in total nitrogen content among the treatments on maize plant parts. Total nitrogen content was recorded as higher under both pot conditions regardless of soil. Both soils showed low total nitrogen content towards the root and leaves under all the treatments and higher N uptake was recorded on grain and stover of nanozeourea. The slow release pattern might be the responsible factor for enhanced nitrogen uptake. Similar results were reported in low land rice [7], sugarcane [21] and the total N uptake in maize[30] plants was obtained highest to lowest as micronutrient coated urea >gelatin + Cu coated urea > Palm stearin + Cu coated urea > Cu coated urea >

Agar + Cu coated urea > uncoated urea, which which were 762, 676, 523, 491, 324 mg pot⁻¹, respectively. Zeolites mixed with chemical fertilizers helped to retain nutrients in root zone and, hence, improving the long term soil quality by enhancing nutrient absorption [32] and [33] application of Nano-chelate levels Increased accumulation of iron, potassium and decreased accumulation of sodium, nitrate and nitro in spinach leaves.

3.7 Yield Parameters

In inceptisol, grain yield was significantly influenced by various N formulations while 100 grain weight was not altered significantly. Zeourea and nanozeourea fertilized maize plants registered significantly higher grain yield per plant. Despite test weight was not significant, higher grain yield was registered in nanozeourea treatment which is comparable to zeourea. Lowest grain yield was registered in zeolite + urea or nano-zeolite + urea treatments. In alfisol, the highest grain yield of 254 g per plant was registered in treatment that received recommended dose of nanozeourea which was 38% higher than conventional urea fertilization. Even zeo-urea fertilized treatment had increased the grain yield to the tune of 31.5%. Same set of

treatments had also registered higher values for 100 grain weight (Table 5).

3.8 Quality Parameters - Crude Protein

Crude protein content of maize grains was the highest in nanozeo urea fertilized plants regardless of light textured or heavy textured soils. Crude protein in the best treatment was 4.9% and 4.7% in black and red soils, respectively (Table 5).

The crude proteins recorded in nanozeo urea treated plants in black and red soils were 26.1% and 36.1%, higher than urea fertilized treatments. The lowest crude proteins recorded in the treatment that received zeolite blended with urea. On yield components the significant differences were observed (Days taken for Tasseling and Silking, hundred grain weight and grain and stover yield) of maize. It may be the effect of slow release and controlled release of nitrogen from the by nanozeourea application and availability of nitrogen throughout crop growth period. The combined application of zeolite and chemical fertilizer increased growth and yield of apple per tree and per unit area. This is in agreement with the findings of [21] application of zeolite and chemical fertilizer

Table 4. Effect of zeolite based N fertilizers on maize N content (%)

Treatments	Inceptisol			Alfisols		
	Root	Stover	Grain	Root	Stover	Grain
T ₁ - Urea	0.26	0.34	0.58	0.25	0.25	0.48
T ₂ - Zeolite +Urea	0.22	0.30	0.53	0.25	0.23	0.52
T ₃ - Nanozeolite + Urea	0.25	0.26	0.62	0.19	0.23	0.52
T ₄ - Zeourea	0.27	0.78	0.62	0.28	0.23	0.59
T ₅ -Nanozeourea	0.32	0.51	0.78	0.28	0.32	0.76
S.Ed	0.02	0.09	0.04	0.02	0.02	0.06
CD (0.05)	0.05	0.18	0.09	0.06	0.04	0.13

Table 5. Effect of zeolite based N fertilizers on maize yield and quality parameters

Treatments	Inceptisol			Alfisols		
	Grain yield (g)	100 grain wt(g)	Crude protein (%)	Grain yield (g)	100 grain wt(g)	Crude protein (%)
T ₁ - Urea	268	27.8	3.62	156	25.8	3.00
T ₂ - Zeolite +Urea	232	28.2	3.32	203	25.4	3.25
T ₃ - Nanozeolite + Urea	238	28.0	3.85	133	25.7	3.22
T ₄ - Zeourea	295	29.3	3.90	173	27.1	3.70
T ₅ -Nanozeourea	291	29.8	4.90	254	29.4	4.70
S.Ed	23.01	1.11	0.28	27.59	1.27	0.41
CD (0.05)	47.00	NS	0.57	56.36	2.60	0.83

improved the sugarcane yield and sweetness (Brix). The nano-subnano composites of kaoline were used as the cementing and coating materials of slow/controlled release fertilizer [34]. The nutrient loaded zeolite (zeopro) improved growth, yield and quality of cucumber and tomato [35]. The mixture of compost and zeolite was enhanced the growth characters, essential oil yield and chemical composition of Achillea plants [36]. Nitrogen fertilizer management of Eggplant and nano-iron chelate foliar spray improved yield and yield components [37].

4. CONCLUSION

Response of maize plants to the fabricated fertilizers were tested two distinct soil textures (Inceptisol – Periyannayakkan palayam soil series – clay loam and Alfisols - Irugur soil series-sandy loam). The grain N content of nanozeourea on inceptisol (Control: 0.26%; Treated 0.32%) and alfisols (Control 0.48; Treated 0.76%) were higher consistently. The response was more pronounced in alfisol than inceptisol. The growth, yield, quality and nutrient uptake were consistently higher for nanozeourea treatment than conventional urea.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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