

# Zeolite- based slow release nanoformulation influencing soil fertility

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## ABSTRACT

A pot culture experiment was conducted to assess the relative performance of fertilizer composites developed using conventional fertilizers and zeolite based nano formulations in the recommended proportions of N, P, K, S, Zn, B and Mo using greengram as test crop. The plants were fertilized with 0, 25, 50, 75 and 100 % of the conventional or nano-fertilizer formulations. Before fortification the Zeolite were subjected to size reduction and modified by using hexadecyltrimethylammonium bromide, a cationic surfactant, to modify its surface to increase its capacity to retain anions. During the experiment soil samples were collected and assessed for its nutrient status besides biochemical properties and microbial population. The result shows that the physical and chemical properties of conventional fertilizer applied and nano-fertilizer formulation applied soils were significantly differs in terms of bulk density, particle density, porosity, pH, EC and CEC. The biochemical properties such as water soluble carbon and biomass carbon then biological properties like microbial populations in soils are measured in end of the experiment shows the significant response to added conventional or nano-fertilizer. Pot culture study also confirms that the soil available nutrients responded well for nano-zeolite. Higher biological activities in nano-fertilizer fertilized soil reached within 25 or 50% of the nanofertilizer in comparison to conventional fertilizer.

**Key words:** Nano-fertilizer, Soil fertility, Zeolite, Fortification

Zeolites are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations, with a three-dimensional lattice, furrowed by an inner network of pores and channels. Zeolites have a high cation exchange capacity and have often been used as inexpensive cation exchangers for various applications (Breck, 1974). Zeolites consist of cage-like polyhedral units with a high cation-exchange capacity and internal pores in crystal lattices that result in high water adsorption and nutrient retention (Faghihian, 2005). Zeolite does not break down over time, but remains in the soil to improve nutrient retention. Therefore, its addition to the soil may significantly reduce water and fertilizer costs by retaining beneficial nutrients in the root zone. The porous structure of natural zeolite helps keep the soil aerated and moist as well as active for a long time. Zeolites increase the water-retention capacity of the soils (Notario del Pino, 1994). The higher the average ionic potential of the extra- framework cations, the larger the hydration capacity of the clinoptilolite. This

trend may be attributed to the small size as well as the efficient water-cation packing of high field strength cations in the zeolite structure (Yang *et al.*, 2001).

Haggerty *et al.* (1994) reported surfactant-modified zeolite (SMZ), a type of inexpensive anion exchanger, to remove anionic contaminants from water. Under the surfactant bilayer configuration, the zeolite reverses its surface charge, resulting in a higher affinity for negatively charged anions, and the sorption and retention of anions are attributed to surface anion exchange. Thus, SMZs offer a great promise as anion carriers for slow release of nutrients. Zeolites increase ion-exchange sites in soils in addition to offering absorption sites for small molecules, due to their porous structure (Muhlbachova, 2003) and studies also confirmed that using natural zeolites have demonstrated significant improvements in fertilizer efficiency. With all these ideas an attempt were made to improve the nutrient use efficiency and use zeolite as a nutrient carrier for slow and steady release of nutrients in soil.

## MATERIAL AND METHODS

### Mechanical synthesis of nano-zeolite (Ball milling)

A ball mill, a type of grinder, is a cylindrical device used in grinding (or mixing) materials like ores, chemicals, ceramic raw materials and paints. The ball milling which was used for the size reduction is FRITSCH – High Energy Ball milling. The vials used for sample loading were stainless steel so the rotating ball taken was also the same material. The zeolite material was taken in 1:20 (sample and ball ratio). Exactly 20g of zeolite sample and 200 g of uniform sized ball was taken and rotated at 400 rpm for 3 hour in 4 half cycle of pause time 15 minutes per 30 minutes interval.

### Fortification of nutrients

As per the recommendation of pulse crop (Greengram) the nutrients such as N, P, K, Zn, S, B, and Mo are fortified into the surface modified zeolite. The sources of nutrients are urea, diammonium phosphate, muirate of potash, zinc sulphate, gypsum, borax and sodium molybdate for N, P, K, Zn, S, B, and Mo, respectively. The nano-composite was developed by loading the entire nutrient in solution form into an exactly weighed 100 g of nano-zeolite. Then the sample was homogenized using ultra sonic system (Sonicator) for exactly 30 minutes at temperature 37<sup>0</sup>C. The sample was shade dried and powdered and it has been used as a fertilizer source.

### Composition of nutrient fortified

Nano-composites were prepared using zeolite, urea, DAP and potassium chloride, Gypsum, borax, sodium molybdate and zinc sulphate. The nano-composites contained 42% N, 35% P<sub>2</sub>O<sub>5</sub> and 52% K<sub>2</sub>O, 15% SO<sub>4</sub>, 30% Zn, 30% MoO<sub>4</sub>, 4.6 % B.

### Particle Size analysis

The zeolite sample after ball milling was taken and tested for particle size analysis. Particle Size Analysis is an analytical technique by which the distribution of sizes in a sample of particulate material can be measured. Particle Size Analyzer (Malvern, Zetasizer Ver.6.01) was used to measure the dimension of the zeolite fortified with or without nutrients. Accurately, 100 mg of zeolite sample was dispersed in 20 ml of acetone and sonicated using ultrasonic processor for twenty minutes at 250 rpm. Then measurements were taken using particle size analyzer. The machine measures the size distribution of the particle and average diameter of the nanoparticles. The soil samples were collected from

Agricultural Research Station, Bhavanisagar and tested for initial soil characteristics. A greenhouse experiment was conducted at Department of Soil Science and Agricultural Chemistry, TNAU, Coimbatore in order to study the relative performance of conventional and nano- fertilizer formulation using greengram (CO7 Variety) as a test crop. The treatments consists of Four levels of Conventional fertilizer and Nano formulation both at the rate of 25, 50, 75 and 100 % of RDF were applied as basal dose. Treatments were replicated three times in factorial randomized block design and one control was maintained without any fertilizer. Fertilizer recommendation was N - 25 Kg ha<sup>-1</sup> (Urea); P - 50 Kg ha<sup>-1</sup> (SSP); K - 25 Kg ha<sup>-1</sup> (MOP); S - 40 Kg ha<sup>-1</sup> (Gypsum); Zn - 25 Kg ha<sup>-1</sup> (ZnSO<sub>4</sub>); B - 1 Kg ha<sup>-1</sup> (Borax); Mo - 0.5 Kg ha<sup>-1</sup> (Sodium molybdate).

### Soil analysis

The Physical properties namely bulk density, particle density and pore space were determined by cylinder method as given by Guptha and Dhakshinamurthi (1980) and water holding capacity (WHC) was determined by Keen Raczkowski brass cup method as given by Piper (1966). The physicochemical properties such as Soil Reaction (pH) and Electrical conductivity (EC) was determined by using 1:2.5 soil water extract as given by Jackson (1973). The chemical properties available Nitrogen of soil was determined by alkaline permanganate method as given by Subbiah and Asija (1956), available phosphorus by 0.5 M NaHCO<sub>3</sub> (pH 8.5) as given by Olsen *et al.* (1954), available potassium by neutral normal ammonium acetate method by Stanford and English (1949), calcium and magnesium by versanate method, available boron by hot water soluble method, available sulphur by turbidimetric method, available micro nutrients by diethylene triamine penta acetic acid (DTPA) method. The Biochemical properties of soil viz., water soluble organic carbon was determined as per the procedure outlined by McGill *et al.* (1975) and biomass carbon was determined by titrating against 0.5 N HCl using phenolphthalein indicators (Jenkinson and Powlson, 1976). The biological properties i.e., microbial population by serial dilution and incubation techniques.

## RESULT AND DISCUSSION

The physical properties of conventional fertilizer applied and nano-fertilizer formulation applied soils were significantly differs in terms of bulk density, particle density, porosity (Table 1.). Highest values were

registered for all the three parameters in control and the values get decreased with incremental levels of fertilizer practices. The lowest values were registered in treatment that received 100% of the either of the fertilization practices. In comparison to conventional fertilizer since the nano-fertilizer are basically zeolite-based which may have helped in improving the physical condition of soil. Liu *et al.* (2006) reported that nanoformulation improve the physical condition of the soil as a result of soil reaction between nano-

composite and natural organic mineral granules. The pH of the nano-fertilizer applied soils was significantly lower than conventional fertilizer applied soils (Table 2.). However, the incremental levels of nano-fertilizer formulation progressively increased. The nano-fertilizer applied soils had significantly lower pH nearly 1 unit in comparison to control. There was a remarkable increase in EC of soils fertilized with incremental levels of conventional fertilizers (Table 2.).

**Table 1. Effect of nanocomposite on soil physical properties**

Treatments	Bulk density (g cm <sup>-3</sup> )		Particle density (g cm <sup>-3</sup> )		Porosity (%)	
	CF	NF	CF	NF	CF	NF
<b>Control</b>	1.23	1.23	2.23	2.23	44	44
<b>25%</b>	1.20	1.21	2.29	2.28	44	44
<b>50%</b>	1.19	1.13	2.34	2.38	46	50
<b>75%</b>	1.15	1.10	2.39	2.47	47	52
<b>100%</b>	1.11	1.07	2.47	2.62	50	52
<b>F</b> SEd	0.003		0.006		0.066	
CD (0.05)	0.007		0.012		0.139	
<b>L</b> SEd	0.005		0.009		0.104	
CD (0.05)	0.011		0.019		0.219	
<b>FL</b> SEd	0.007		0.013		0.148	
CD (0.05)	0.015		0.027		0.311	

**Table 2. Effect of nanocomposite on soil chemical and biochemical properties**

Treatments	pH		EC (dSm <sup>-1</sup> )		Soil CEC (c mol (p <sup>+</sup> ) kg <sup>-1</sup> )		Water soluble organic carbon (%)		Biomass carbon (mg <sup>-1</sup> Kg)	
	CF	NF	CF	NF	CF	NF	CF	NF	CF	NF
<b>Control</b>	7.59	7.59	0.21	0.56	7.9	7.9	0.56	0.56	1274.6	1274.6
<b>25%</b>	7.21	6.19	0.80	0.33	11.9	13.6	0.33	1.31	1037.5	1579.5
<b>50%</b>	7.34	6.65	0.88	0.56	14.0	17.2	0.56	1.40	1231.1	1728.0
<b>75%</b>	7.39	6.69	0.67	1.03	15.0	24.9	1.03	1.85	1377.8	2422.6
<b>100%</b>	7.45	6.67	1.10	1.11	17.0	28.2	1.11	1.30	1728.6	2069.8
<b>F</b> SEd	0.019		0.007		0.012		0.023		1.51	
CD (0.05)	0.041		0.016		0.024		0.049		3.17	
<b>L</b> SEd	0.031		0.011		0.018		0.037		2.38	
CD (0.05)	0.065		0.025		0.039		0.077		5.01	
<b>FL</b> SEd	0.044		0.017		0.026		0.052		3.37	
CD (0.05)	0.092		0.035		0.055		0.109		7.09	

The EC had increased by 4-5 times in conventional fertilizer applied soils in comparison to the control. Such an increase was also observed in treatments that received nano-fertilizer composites. The CEC of the nano-fertilizer applied soil where

consistently higher at all levels of fertilization (Table 2.). The increase in CEC is more pronounced under 75 or 100% fertilization level than the other levels. The reduction in soil pH may be attributed to the retention of cations that may have adsorbed on the

sheet of zeolite leave more H<sup>+</sup> ion activity in the soil solution. In contrast, other studies have shown an increase in pH as a result of zeolite additions (Noori *et al.*, 2006). Our study indicated that the EC had increased slightly when nano-fertilizer was applied at 100%. Ming and Boettinger (2001) reported that the application of zeolites to soils increases their EC, and as a result, it increases nutrient retention capacity. Our data are in agreement with the observation of Stead (2010) who reported that zeolites have been shown to increase the soil cation exchange capacity.

The biochemical properties such as water soluble carbon and biomass carbon are measured in end of the experiment shows the significant response to added conventional or nano-fertilizer (Table 2.). The water soluble carbons estimated in nano-fertilizer fertilized soils were significantly higher by 4 and 3 times as that of conventional fertilizer soils at 25% conventional for applied soil for all the three macronutrients namely nitrogen, phosphorus and potassium (Table 3.). The increase in available nitrogen in nano-fertilizer fertilized soils increased with corresponding increase in quantities of fertilizer applied (Fig.1). The available N status was initially categorized as low and remained low in conventional applied soils in all the levels of application while the nano-fertilizer fertilized soil especially 50%, 75% and 100% nano-fertilizer fertilized soil registered medium status of available nitrogen. Similar to nitrogen available phosphorus also increased with incremental levels of both CF and NF fertilization (Fig 2.).The average increase in available phosphorus status was 2- 2.4 Kg ha<sup>-1</sup> till 75% of CF or NF fertilizer applied.

and 50% respectively. Such pronounced response was not seen at 75% or 100% of the recommended dose of fertilization irrespective of conventional fertilization. The data on water soluble carbon closely coincided with biomass carbon. An active pool of carbon measured in terms of biomass carbon was significantly higher in nano-fertilizer fertilized soil at all levels of fertilization. The increase in biomass carbon of nano-fertilizer fertilized soil at 25%, 50%, 75% and 100% were 34.3, 28.7, 43.1, and 16.4, respectively. The data closely coincide with the observation of Paramanathan (2000) and Subramanian and Rahale (2009). The available nutrient status of nano-fertilizer applied soil were significantly higher than conventional for applied soil for all the three macronutrients namely nitrogen, phosphorus and potassium (Table 3.).

At the 100% level both CF and NF registered the same values of 20.3 Kg ha<sup>-1</sup>. The response to nano-fertilizer application was relatively smaller for available K status (Fig 3.). The available potassium showed an increase at 50% and 75% of doses of conventional or nano-fertilizer application. There was a significant lower in available potassium status was detected at 25 and 100% dose in nano-fertilizer fertilized soil in comparison to conventional fertilized soils. Perez-Caballero *et al.* (2008) reported that zeolite has the capacity to reduce nitrate and ammonium from leaching treatments with zeolite improved P, K and Ca concentrations in the soil because the zeolite also has the ability to absorb these nutrients from the fertilizers used as well as reducing

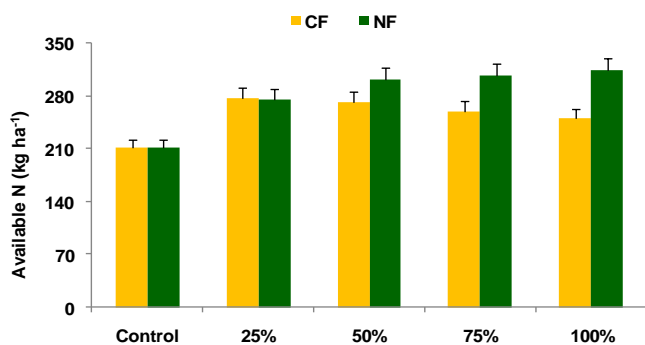
**Table 3. Effect of nanocomposite on available nitrogen, phosphorus and potassium contents of soil**

Treatments	Nitrogen (Kg ha <sup>-1</sup> )		Phosphorus (Kg ha <sup>-1</sup> )		Potassium (Kg ha <sup>-1</sup> )	
	CF	NF	CF	NF	CF	NF
<b>Control</b>	211.5	211.5	18.4	18.4	230.7	230.7
<b>25%</b>	276.8	276.3	17.3	19.7	226.8	222.7
<b>50%</b>	272.3	302.3	17.5	19.9	230.4	236.9
<b>75%</b>	260.4	307.2	17.6	20.4	234.0	246.0
<b>100%</b>	251.2	314.0	20.3	20.3	240.7	233.7
<b>F</b> SEd	1.29		0.06		0.47	
CD (0.05)	2.72		0.12		0.99	
<b>L</b> SEd	2.05		0.09		0.75	
CD (0.05)	4.31		0.18		1.57	
<b>FL</b> SEd	2.90		0.12		1.06	
CD (0.05)	6.09		0.26		2.22	

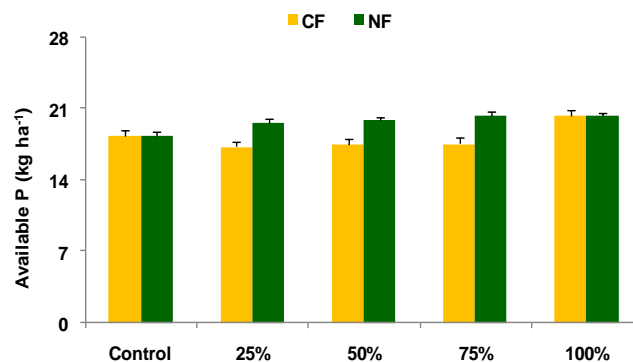
leaching in the soil. Increase in soil pH due to zeolite application may have also contributed to these

nutrients availability in the soil. Milosevic and Milosevic (2009) reported that zeolite in combination

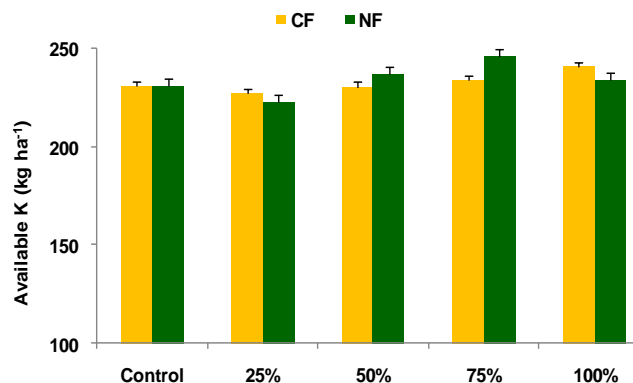
with mineral NPK fertilizer containing 15% K enhanced the available K status in the soil. The available status of secondary nutrients such as calcium, magnesium and sulphur had progressively and significantly increased with an incremental levels of conventional or nano-fertilizer fertilization (Table 4.). However, nano-fertilizer applied soils has consistently higher values than conventional fertilizer applied soils. All the three secondary nutrients showed a significant reduction in their availability especially when 100% recommended levels of fertilizer in the form of nano-fertilizer formulation when compared to conventional fertilizer. In available status of sulphur nano-fertilizer application at the status of 25% indicated a reduction in available status in comparison to conventional fertilizer (Fig 4.). Mazur *et al.* (1986) pointed out that zeolite improved calcium and magnesium in the soil. These observations were comparable with those reported by other authors (He *et al.*, 2002; Huang and Petrovic, 1994). (Perez-Caballero *et al.*, 2008) reported that treatments with zeolite improved P, K and Ca concentrations in the soil because zeolite had the ability to absorb these nutrients from the fertilizers used as well as reducing leaching in the soil. Li and Zhang (2005) indicated that SMZ could be a good carrier for sulfate. Thus, leaching of sulfate can be greatly reduced and slow release of sulfate can be achieved if SMZ is used as fertilizer additives. Mazur *et al.* (1986) pointed out that zeolite improved calcium and magnesium in the soil. These observations were comparable with those reported by other authors (He *et al.*, 2002; Huang and Petrovic, 1994). Perez-Caballero *et al.*, 2008 reported that treatments with zeolite improved P, K and Ca concentrations in the soil because zeolite had the ability to absorb these nutrients from the fertilizers used as well as reducing leaching in the soil.



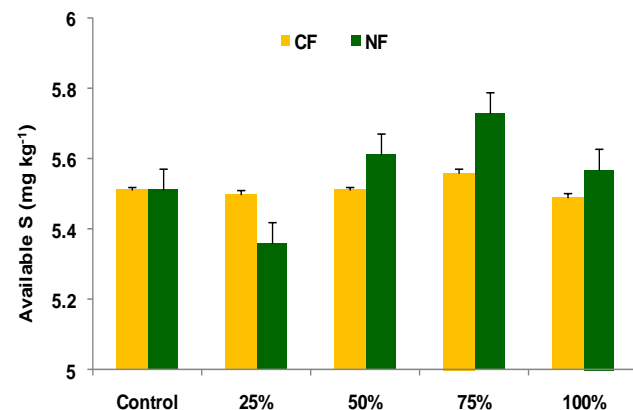
**Fig 1. Effect of nanocomposites on available nitrogen content of soil**



**Fig 2. Effect of nanocomposites on available phosphorous content of soil**



**Fig 3. Effect of nanocomposites on available potassium content of soil**



**Fig 4. Effect of nanocomposites on available sulphur content of soil**

Li and Zhang (2005) indicated that SMZ could be a good carrier for sulfate. Thus, leaching of sulfate can be greatly reduced and slow release of sulfate can be achieved if SMZ is used as fertilizer additives. Mazur *et al.* (1986) pointed out that zeolite improved calcium and magnesium in the soil. The nano-fertilizer application significantly increases the available Fe, Mn, Cu, Zn and B (Table 5.). The increase in availability increased NF with incremental

levels of application regardless of fertilizer formulations. The NF fertilizer application had a more profound effect on available Fe, Mn, Cu, Zn and B than conventional fertilizer application. The available Fe status maintained close to the initial

values of 41.6 mg kg<sup>-1</sup> in CF applied soils while NF fertilizer applied soil had 2- 3 mg higher values where obtained. The available Zn was significantly higher in 50% and 75% nano-fertilizer fertilized treatment in respect to conventional fertilizer fertilization (Fig 5.).

**Table 5. Effect of nanocomposite on available boron, Fe, Zn, Mn and Cu contents of soil**

Treatments	Fe (mg kg <sup>-1</sup> )		Zn (mg kg <sup>-1</sup> )		Mn (mg kg <sup>-1</sup> )		Cu (mg kg <sup>-1</sup> )		Boron (mg kg <sup>-1</sup> )	
	CF	NF	CF	NF	CF	NF	CF	NF	CF	NF
<b>Control</b>	41.6	41.6	1.53	1.53	12.36	12.36	3.15	3.15	0.19	0.19
<b>25%</b>	39.7	40.8	1.55	1.52	12.09	12.12	3.14	3.38	0.21	0.22
<b>50%</b>	39.8	41.5	1.56	1.58	12.22	12.48	3.19	3.57	0.22	0.24
<b>75%</b>	40.8	43.1	1.59	1.72	12.26	12.75	3.26	3.61	0.24	0.26
<b>100%</b>	41.4	43.3	1.66	1.61	12.40	12.97	3.34	3.73	0.25	0.24
<b>F</b> SEd	0.082		0.009		0.026		0.016		0.002	
CD (0.05)	0.174		0.019		0.056		0.033		0.004	
<b>L</b> SEd	0.131		0.014		0.042		0.025		0.003	
CD (0.05)	0.275		0.041		0.088		0.053		0.007	
<b>FL</b> SEd	0.185		0.020		0.053		0.036		0.004	
CD (0.05)	0.389		0.042		0.125		0.075		0.009	

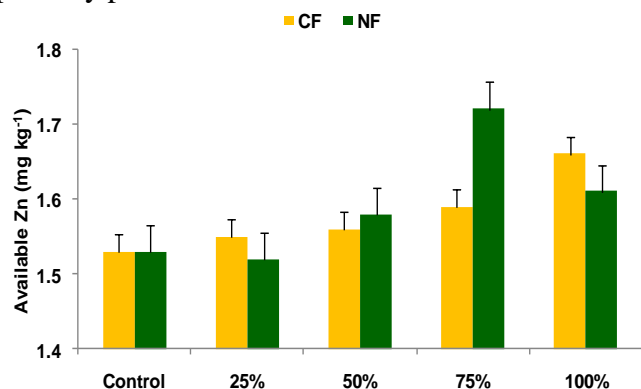
**Table 6. Effect of nanocomposites on biological properties of soil**

Treatments	Fungi (10 <sup>4</sup> )		Bacteria (10 <sup>6</sup> )		Actinomycetes (10 <sup>3</sup> )	
	CF	NF	CF	NF	CF	NF
<b>Control</b>	32	32	43	43	14	14
<b>25%</b>	37	43	45	48	16	22
<b>50%</b>	39	46	47	52	19	23
<b>75%</b>	40	48	50	55	22	26
<b>100%</b>	45	49	52	56	25	28
<b>F</b> SEd	0.19		0.19		0.22	
CD (0.05)	0.41		0.39		0.46	
<b>L</b> SEd	0.31		0.30		0.35	
CD (0.05)	0.65		0.63		0.73	
<b>FL</b> SEd	0.44		0.42		0.49	
CD (0.05)	0.92		0.89		1.03	

There was a significant reduction in available Zn status when fertilizer applied in 100% NF in comparison to respective conventional fertilizer. Available Mn and Cu status showed higher values of nano-fertilizer fertilization irrespective of levels of fertilization. Available hot water soluble boron showed a linear increase in both CF and NF fertilized

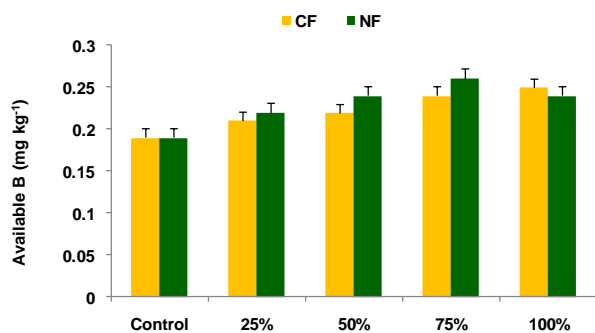
soils but the linearity existed only upto 75% in nano-fertilizer fertilized soils (Fig 6.). Markus and Othmar (2003) reported on the influence of fertilization with slow release zeolite-bound zinc and copper on the cadmium uptake of wheat and spinach. He reported that application of Zn zeolite resulted in a reduction of about 10% of the Cd level in wheat straw relative

to the control. Sheta *et al.* (2003) research was undertaken to characterize the ability of five natural zeolites and bentonite minerals to adsorb and release zinc and iron. Broos *et al.* (2007) reported that the slow release of Zn is attributed to the sparingly solubility of minerals and sequestration effect of exchanger, there by releasing trace nutrients to zeolite exchange sites where they are more readily available for uptake by plants.



**Fig 5. Effect of nanocomposites on available zinc content of soil**

Soil microbial population enumerated at the harvest stage showed a phenomenal increase in bacteria, fungi and actinomycetes with incremental levels of fertilizer application in both conventional and nano-fertilizer formulation (Table 6.). The highest number of microbial colonies was registered at 100% RDF applied in the form of nano-fertilizer formulation at  $49 \times 10^4$ ,  $56 \times 10^6$  and  $28 \times 10^3$  for fungi, bacteria and actinomycetes respectively.



**Fig 6. Effect of nanocomposites on available boron content of soil**

The values for the conventional fertilizer were  $45 \times 10^4$ ,  $52 \times 10^6$  and  $25 \times 10^3$  indicating a significantly lower value. Higher biological activities in nano-fertilizer fertilized soil reached within 25 or 50% of the NF in comparison to CF. Liu *et al.* (2006) also reported that nano-composites promoted the action of microorganisms. Navrotsky (2004) reported that the

physico-chemical properties in the surface of nano-composites provided much of reactivity to soil biological and abiotic processes. Andronikashvili (2008) reported that introduction of clinoptilolite containing tuffs into soils has positive effect on bacteria, fungi and actinomycetes population. Vestberg (2008) reported that zeolite when mixed with soil, increased the arbuscular mycorrhizal fungi colonization in greenhouse experiments. Vosatka and Gryndler (2000) reported that zeolite has positive effect on AM colonization in potato crop. The pot culture studies confirmed that the nano-composite can be effectively used as a slow release fertilizer where the nutrients, biochemical properties has been improved for the nano-composite treatment.

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