



## RESEARCH ARTICLE

## Role of nano-fertilizer on Greenhouse Gas Emission in Rice Soil Ecosystem

Mohanraj. J\*<sup>1</sup>, Subramanian. K.S<sup>2</sup> and Lakshmanan. A<sup>1</sup>

<sup>1</sup>Department of Nano Science and Technology, Tamil Nadu Agricultural University, Coimbatore - 641 003.

<sup>2</sup>Director of Research, Tamil Nadu Agricultural University, Coimbatore - 641 003.

### ABSTRACT

The mitigation of greenhouse gases from rice soils is one of the potential strategies to minimize the impact of climate change. This study focuses on the application of nano-zeolite based nitrogenous fertilizer in order to slow down the release of N from the fertilizer to reduce the emission of GHGs mainly methane. Nano-fertilizer carrying  $\text{NO}_3^-$  or  $\text{NH}_4^+$  forms of nitrogen were synthesized using commercial nano-zeolite by fortifying two forms of N. Nitrogen release from the nano-zeolite loaded with (Nitrate and ammonical form of N) were studied in percolation reactor. The data have shown that N release from the nano-fertilizer ( $\text{NO}_3^-$  or  $\text{NH}_4^+$ ) forms of N were 11.6 and 20 days, respectively. While N release from conventional forms potassium nitrate and ammonium sulfate fertilizers were 8.7 and 12.9 days, respectively. Consequently, nano-fertilizer applied rice soil had lower  $\text{N}_2\text{O}$  emission of (1.8) than conventional fertilizer ( $2.7 \text{ mg m}^{-2} \text{ day}^{-1}$ ). One of the striking effects was on methane emission was lower in nano-fertilizer applied soil (34.8) than control ( $36.8 \text{ mg m}^{-2} \text{ day}^{-1}$ ). These data clearly suggest that the nano-fertilizer assists in slow release of nitrogen that eventually resulted in reduction of emission of greenhouse gases ( $\text{CH}_4$  &  $\text{N}_2\text{O}$ ) from the rice soil ecosystem.

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### INTRODUCTION

Rice soils are prone to greenhouse gas emissions mainly methane and nitrous oxide under submergence. Asian countries including India are blamed for the excessive production of greenhouse gases causing climate change and associated ill-effects. An increasing amount of greenhouse gases (GHGs) in the atmosphere is becoming a very serious thing to the depredation of human livelihood as well as natural landscape. The rice soils act the biggest contributor to greenhouse gas emission responsible for 20% of the world. (Adhya *et al.* 2000). Climate change due to the increased atmospheric concentration of greenhouse gases (GHGs) is a cause for concern worldwide. Irrigated rice farming is a significant anthropogenic source of  $\text{CH}_4$  and nitrous oxide and anaerobic decomposition of organic material in flooded rice fields produce methane ( $\text{CH}_4$ ), which escapes to the atmosphere primarily by diffusive transport through the rice plants during the growing season. The Intergovernmental Panel on Climate Change (IPCC, 1996) estimated the global emission rate of methane from paddy fields at  $60 \text{ Tg/yr}$ , with a range of 20 to  $100 \text{ Tg/yr}$  with 5-20 per cent of the total

emission from all anthropogenic sources. Nitrous oxide is emitted when nitrogen is added to the soil through the use of synthetic fertilizers. Nitrous oxide is also emitted during the breakdown of nitrogen in livestock manure and urine, which contributed to 5% of  $\text{N}_2\text{O}$  emissions in 2011.

One of the potential factors causally related to the greenhouse emission in wetlands is attributed to the use of nitrogenous fertilizers (Rajkishore *et al.*, 2015). Nitrogenous fertilizers are vulnerable for the loss of N due to leaching, volatilization, and immobilization that collectively contribute up to 60%. In order to reduce the loss of N and improve the N use efficiency, nano-fertilizers hold a promise and the benefits of nano-fertilizers have been reviewed (Subramanian *et al.*, 2015; 2018). Since > 95 % of the Indian soils are deficient in N (Tarafdar, 2016) and the N use efficiency of crops hardly exceeds 30-35% (Oik, 1999), nano-fertilizers may be ideal for Indian soils to improve the use efficiency while minimizing the greenhouse gas emissions. Nano-fertilizers are capable of holding bountiful of nutrient ions due to their high surface area and release it slowly and steadily that commensurate with crop demand. Subramanian *et al.* (2008) reported

\*Corresponding author's e-mail: kssubra2001@rediffmail.com`

that nano-fertilizers and nanocomposites can be used to control the release of nutrients from the fertilizer granules so as to improve the nutrient use efficiency while preventing the nutrient ions either get fixed or lost to the environment (Pereira, Minussi, da Cruz, Bernardi, & Ribeiro, 2012). Nano-fertilizers deliver nutrients in a timely manner to a rhizospheric target with a minimum loss. Fertilizer particles coated with nano-membranes that facilitate in a slow and steady release of nutrients. This process helps to reduce the loss of nutrients while improving the fertilizer use efficiency of crops. Nano-composites are known to nourish the plants with all essential nutrients that ensure balanced fertilization. Zeolites are potential adsorbent due to the ability of their mesoporous structures to adsorb molecules at relatively low pressure. They have been used extensively in industries as adsorbent and the availability of internal space volume is another interesting characteristic of zeolites for developing nitrogen nano-fertilizer. (Subramanian *et al.* 2008). The zeolite-based nano-fertilizers are known to improve both macro and micronutrients use efficiencies (Subramanian and Sharmila, 2013; Manikandan and Subramanian, 2017; Thirunavukkarasu and Yuvaraj, 2017; Subramanian *et al.*, 2018).

Hypothesized that nano-fertilizer application assists in slow release of nitrate and ammonia cal N thereby it improves the N use efficiency by rice while reducing the emission of greenhouse gases.

## **MATERIAL AND METHODS**

### **Nano-fertilizer synthesis**

The nano-zeolite was purchased from M/s Singhal Chemicals, Ahmadabad, Gujarat, used for this study. Two forms of N namely  $\text{NO}_3^-$  and  $\text{NH}_4^+$  forms were fortified in the zeolite substrate. Zeolite otherwise referred to as molecular sieves and nanostructured honeycomb aluminosilicate compound. It can available on s (Manikandan, Subramanian, & Kannaiyan, 2013) synthetically as well as naturally occurring material. Zeolite possessing negative charge on its surface, which had to be surface modified by cationic surfactant hexadecyltrimethylammonium bromide (HDTMABr from Sigma Aldrich, Bangalore), was used for fortification of nitrate ions on the adsorptive sites. (Bansiwal, 2006).

### **Surface modification of nano zeolite**

The negative charge of the nano-zeolite was modified by treating them with a surfactant hexadecyltrimethylammonium bromide as suggested by Bansiwal *et al.* (2006). A pre-weighed quantity of nano-zeolite was mixed with HDTMABr solution in a 1:100 (solid: liquid) ratio. The solution was agitated

for 7-8 h at 150 rpm in ultra-centrifuge. Thereafter, filtered, and the solid residue was washed with double -distilled water and air-dried for 4-6 h. The synthesized surface-modified nano-zeolite was ground with a pestle and mortar to fine particle size.

### **Characterization of nano-fertilizer**

In the present study, nano-fertilizer was loaded with  $\text{NO}_3^-$  and  $\text{NH}_4^+$  forms ions were characterized before and after the loading of nutrients. HORIBA- (SZ-100 Japan) Nano Particle Size Analyzer (also known as Dynamic Light Scattering System) instrument of Beckman Coulter was used to measure the particle size of the before and after loading Nitrogen Ions of nano-zeolite. Zeta potential measurement for nano-zeolite and surface modified nano-zeolite was determined using a zeta analyzer (Horiba, SZ-100). The SEM (Quanta 250, FEI, Netherlands) was used to get the shape of the nutrient-loaded nano-zeolite. SEM analysis to make proper resolution was done by sputtering using gold nanoparticle as a carrier of helium gas coated over the substrate. The SEM is also capable of performing selected point locations on the sample this is especially useful in qualitatively determining chemical compositions (using EDAX).

The crystallinity of N ions loaded nano-zeolite was studied with the help of anrigagu instrument using Cu  $\text{K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The scans were recorded from  $30^\circ$  to  $80^\circ$  at 295k. The functional groups were identified by Fourier transform infrared spectroscopy studies by JASCO -FT/IR - 6800 in the range of  $4000\text{-}400\text{cm}^{-1}$ . The multi-nutrient composite loaded electrospun nanofibres were directly kept into the sample holder with a diamond probe analyzed by the ATR method.

### **Percolation reactor study**

The percolation reactor designed for a continuous flow of nutrient leachate from zeolites was used (Hemandezet *et al.*, 1992). In this reactor, nutrient detainment and controlled release nutrient from the carrier as well as a nutrient from the soil column, can be accurately quantified. The percolation reactor consists of a Teflon tube (internal diameter= 2.5 cm, height = 15 cm) through the top of column deionized water is continuously pumped at a flow rate of 24 ml per day. The inner column of the percolation reactor, 5 g of sieved experimental soil inlay with the nano-fertilizer were placed. Solutions collected to determine ammonium and nitrate ions. The mean temperature during the experiment was  $25 \pm 0.2^\circ\text{C}$ .

### **Pot Experiment**

A pot experiment was conducted at the Agro-Climatic Research Centre (ACRC), Tamil Nadu Agricultural University, Coimbatore. Rice seedlings

(cultivar white ponni) were transplanted into plastic tubs (length x width x height: 1.4m x 0.8m x 0.5m). The fiber tubs were split by 30 cm deep stainless steel metal plates to create 6 sub-plots (70cm x 25 cm). Each sub-plot had nine plants. Each fiber tubs filled with 750 kg of wetland field soil and irrigated water up to a depth of 2.5 cm. A recommended dose of fertilizer 50:50 kg PK ha<sup>-1</sup> applied to the experimental crop uniformly to all the sub-divided treatment plots. The entire dose of P (31.3 g / 250 kg of soil) in the form of single super phosphate (16 %) was applied as a basal dose. Potassium in the form of applied by muriate of potash (60 per cent K<sub>2</sub>O) was applied in four equal splits. Nitrogen was applied in the form of zeolite bases NO<sub>3</sub><sup>-</sup> (6.2%N) and zeolite-based NH<sub>4</sub><sup>+</sup>-N (12.6%N). Each subplot was fertilized accordingly to the N content of fertilizer formulation.

#### Measurement of methane and nitrous oxide

Methane and nitrous oxide emission fluxes from the experimental plots were measured by a closed chamber method of Saha *et al.* (2017) at regular intervals from transplanting to harvest. Samplings for CH<sub>4</sub> and N<sub>2</sub>O fluxes were done at 09:00-10:00 hours and 15:00-16:00 hours and the average of morning and evening fluxes were used as the flux value for the day. For measuring CH<sub>4</sub> and N<sub>2</sub>O fluxes, eleven rice hills were covered with a locally fabricated transparent acrylic sheet chamber (59.3 cm length, 59.3 cm width and 87.8 cm height). (Yan, Yagi, Akiyama, & Akimoto, 2005) A battery-operated fan was fixed for air circulation (avoid plant suffocation) to mix the air inside the chamber and draw the air samples into air-sampling bags (Tedlar®). The air samples from the sampling bags were analyzed for CH<sub>4</sub> and N<sub>2</sub>O fluxes. Each chamber was placed on the soil surface with 4-5 cm inserted into the soil, 10 minutes prior to each sampling for equilibration to reduce the disturbance to the sampling site. The CH<sub>4</sub> and N<sub>2</sub>O were estimated in a Shimadzu GC-2014 gas chromatograph equipped with FID. The gas samples were introduced into the analyzer by filling the fixed loop (1.0 ml) on the sampling valve. Samples were injected into the column system by starting the analyzer which automatically activated the valve and back flush the samples according to the time programmed. The GC was calibrated before and after each set of measurements using CH<sub>4</sub> and N<sub>2</sub>O standards (Chemtron® science laboratories Pvt. Ltd., Mumbai)(Garcia & Barbas, 2011).

## RESULTS AND DISCUSSION

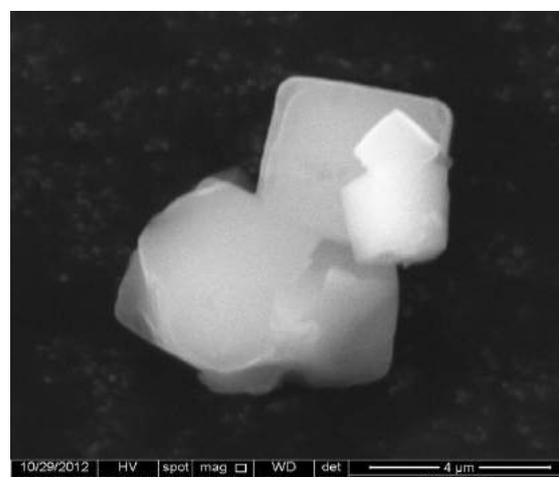
The morphological features of nano-zeolite before and after fortification of nutrients were represented (Table-1). The average size of the particle size distribution was determined in a DLS particle size analyzer. From DLS the average size

of the nano-zeolite showed a particle size diameter between 7-15 nm. The particle distributions of the DLS determined that 90% of the particles under the nano-dimensions.

**Table 1. Characteristics of nano-zeolite (NZ), surface modified nano-zeolite (SMNZ), and nitrate loaded SMNZ and ammonium loaded NZ**

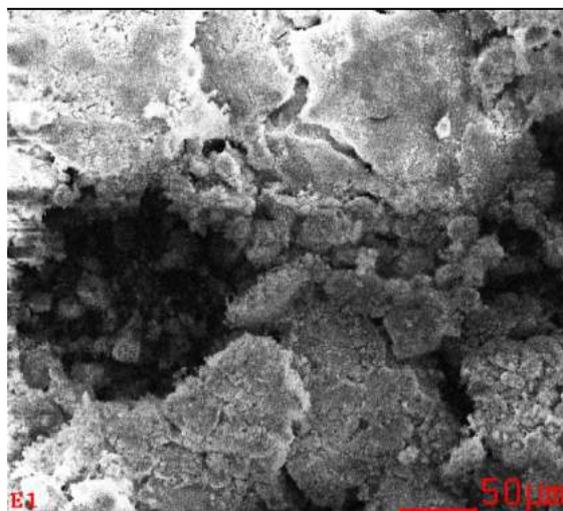
Parameters	NZ	SMNZ	NO <sub>3</sub> <sup>-</sup> -SMNZ	NH <sub>4</sub> <sup>+</sup> -NZ
Size (nm)	7.6	60	66	70
Zeta potential (mV)	-42	+1	-1	-30
Shape	Cubical	Irregular	Irregular	Irregular
CEC (cmol p+ kg <sup>-1</sup> )	270	270	220	220
SiO <sub>2</sub> / Al <sub>2</sub> O <sub>3</sub> ratio	2.0	2.0	1.83	1.83

The zeta potential of dispersed raw nano-zeolite was -42 mV and after nano-zeolite surface modified with cationic surfactant hexadecyltri methyl



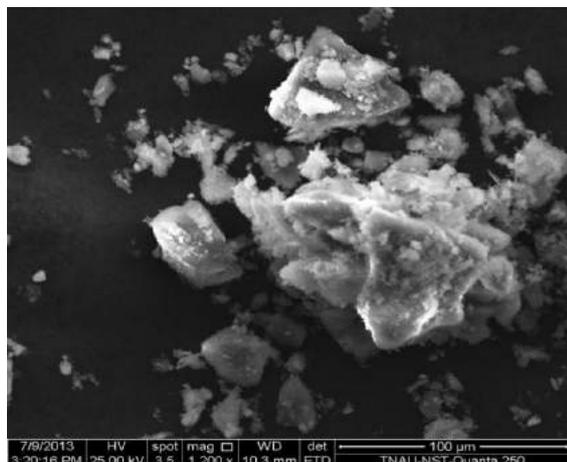
**Figure 1.a. SEM image of the nano-zeolite**

ammonium bromide (HDTMABr) shows +1 mV at 67 mM concentration. The same report can be reported by Subramanian and Sharmila Rahale (2009).



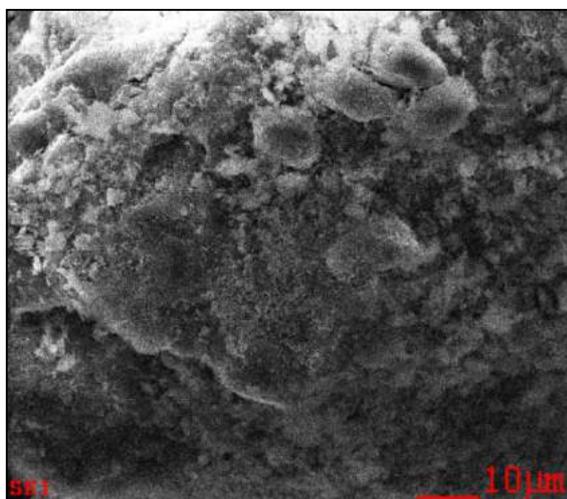
**Figure 1.b. SEM image of the nano-zeolite After loading of NH<sub>4</sub><sup>+</sup>-N**

The SEM characterization showed a cubical structure of raw nano-zeolite, which takes irregular shape after N-loading. The change in morphology might be due to the adsorption of N in raw nano-zeolite (Fig. 1a-d).



**Figure 1c. SEM image of the Surface Modified nano-zeolite**

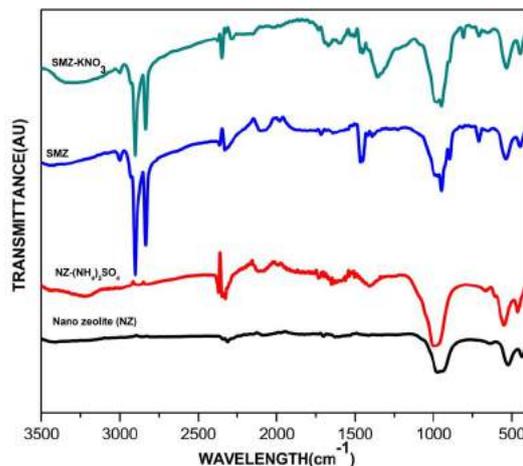
Further, the CEC of nano zeolite reduced from 270(c mol(p) Kg<sup>-1</sup> to 220 (c mol (p+) kg<sup>-1</sup>) when loaded with N due to the presence of either NO<sub>3</sub><sup>-</sup> or NH<sub>4</sub><sup>+</sup>. The SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of nano-zeolite and N-loaded nano zeolite observed 2.0 and 1.83, respectively (Table-1).



**Figure 1d. SEM image of the Surface Modified nano-zeolite NO<sub>3</sub><sup>-</sup> - N**

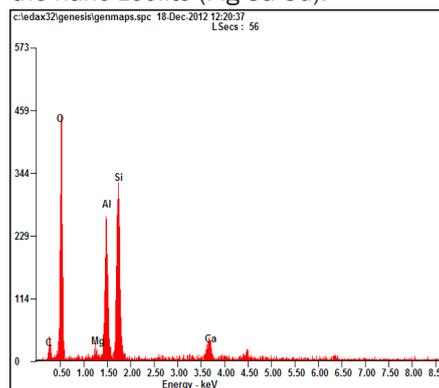
The FT-IR analysis revealed that incorporation of loading of both NH<sub>4</sub><sup>+</sup> - N and NO<sub>3</sub><sup>-</sup> - N in nano - zeolite (Fig.2). The presence of peak located at 3695.61, 2854.65, 2924.09, 1442.75,752 and 551 cm<sup>-1</sup> could be observed in the pure nano-zeolite besides after loading into NH<sub>4</sub><sup>+</sup> - N into nano - zeolite FT-IR spectra showed some peaks located at 1870.95 and 1809.23 cm<sup>-1</sup>, which corresponding to the NH<sub>4</sub><sup>+</sup> - N present in the nano-zeolite. The IR pattern of SMNZ loaded with NO<sub>3</sub><sup>-</sup> - N showed characteristic

peaks at wavenumbers 3691.75, 3630.03, 2519.03, 1870.95, 999.13 and 424.34 cm<sup>-1</sup>. besides the peaks at 1870.95 and 1809.23 cm in NO<sub>3</sub><sup>-</sup> - N loaded SMNZ.

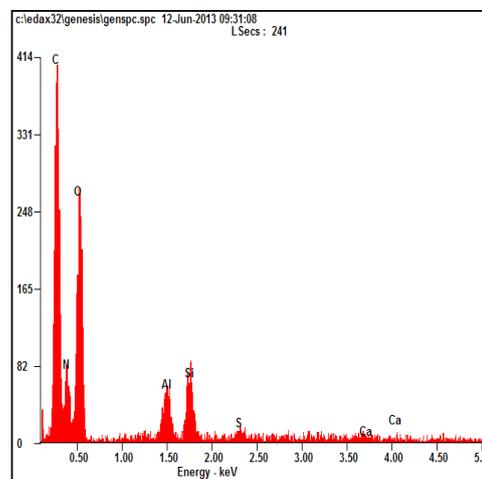


**Figure 2. FTIR spectra of Nano zeolite, Nano Zeolite + Ammonium Sulphate, Surface Modified Zeolite, and SMZ+ Potassium nitrate**

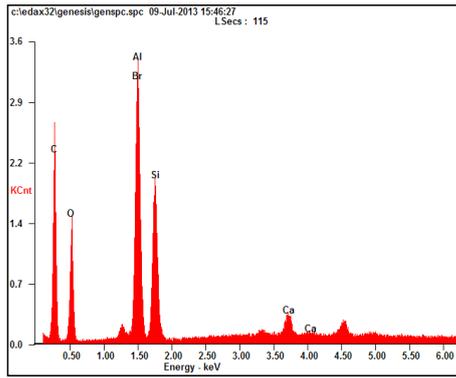
The EDX (Energy-dispersive X-ray spectroscopy) showed the adsorption property of NH<sub>4</sub><sup>+</sup> - N, NO<sub>3</sub><sup>-</sup> - N into the nano-zeolite (Fig 3a-3d).



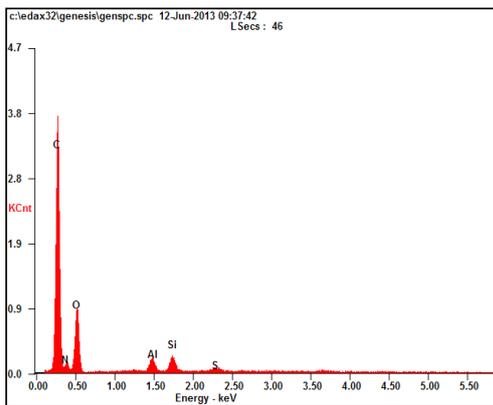
**Figure 3a.EDAX -nano-zeolite before loading nitrogen**



**Figure 3b.EDAX- nano-zeolite after loading with NH<sub>4</sub><sup>+</sup>-N ions**

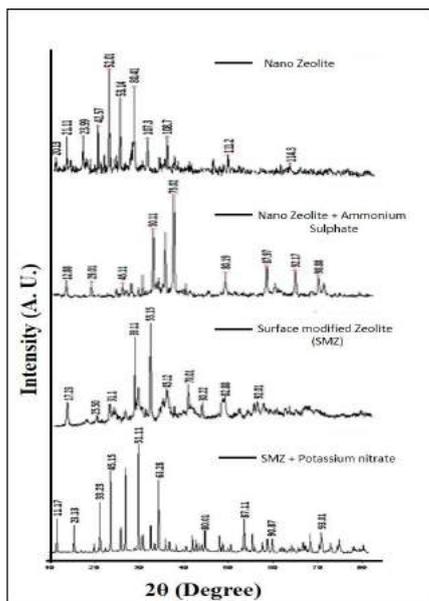


**Figure 3c.EDAX Spectra of surface modified of nano-Zeolite**



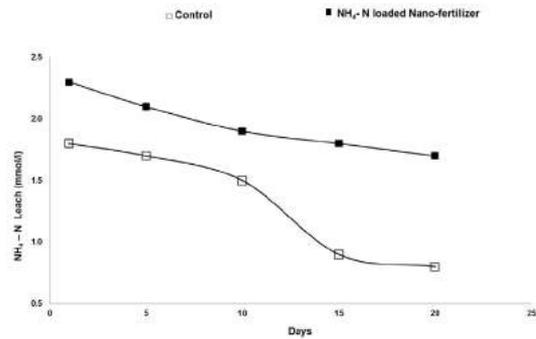
**Figure 3d.EDAX Spectra of nano-zeolite after loading with NO<sub>3</sub>-Nitrogen**

Elemental composition of pure nano-zeolite be composed of carbon (11.74%), oxygen (44.79%), magnesium (8.18%), aluminium (4.66%), silica (26.19%) and calcium (4.43%).



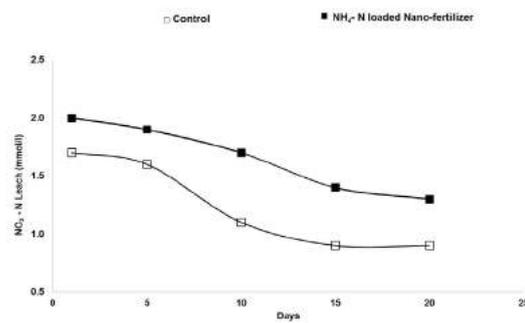
**Figure 4. XRD pattern of (A) Nano zeolite, (B) Nano Zeolite + Ammonium Sulphate, (C) Surface Modified Zeolite, and (D) SMZ+ Potassium nitrate**

The EDX pattern of NH<sub>4</sub><sup>+</sup>-N loaded zeolite shows 10.2 % of the nitrogen content. Whereas NO<sub>3</sub><sup>-</sup> a form of N loaded with SMNZ shows 7.2% of the nitrogen adsorbed by the internal pore of the SMNZ.



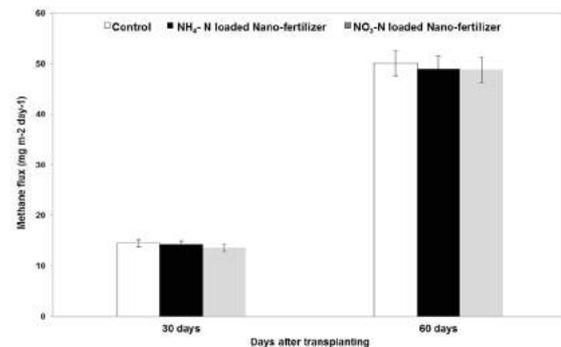
**Figure 5. NH<sub>4</sub>-N release from the soil fertilized with Conventional and Nano-Fertilizers**

The XRD diffraction pattern of pure nano zeolite (Fig.4) shows the strong diffraction peak with 2θ values of 17.23°, 25.50°, 31.10°, 39.11°, 45.12°, 55.15° and 70.01°.



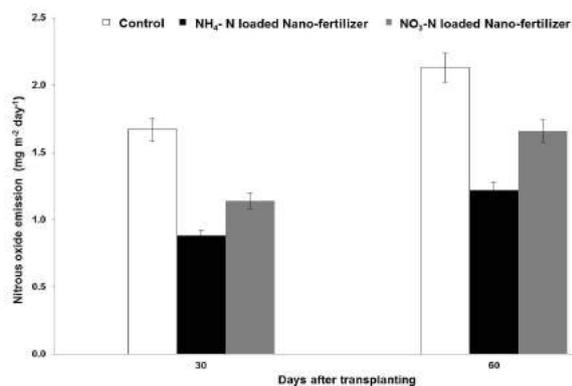
**Figure 6. NO<sub>3</sub>-N release from the soil fertilized with Conventional and Nano-Fertilizers**

When it was loaded with NH<sub>4</sub><sup>+</sup> form of N into the nano-zeolite diffraction peak with 2θ values changes over corresponding to the ammonium sulfate 12.88°, 29.01°, 45.11°, 50.11°, 75.02°, 80.19°, 80.77°(Qion *et al.*, 2007).



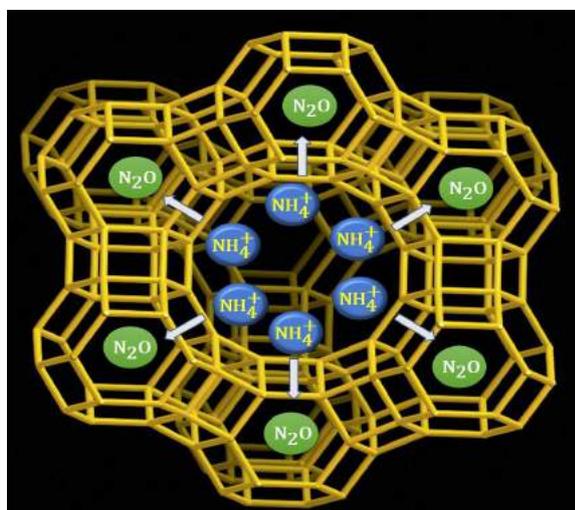
**Figure 7. Nitrous oxide emission (mg m<sup>2</sup> day<sup>-1</sup>) from the soil fertilized with NH<sub>4</sub>-N and NO<sub>3</sub>-N Nano-Fertilizer to Rice (At 5% level p value =0.035 and SD-Error bar)**

In the other hand, SMNZ was loaded with  $\text{NO}_3^-$  form of N few unique peaks were identified from the XRD  $2\theta$  diffraction pattern  $10.72^\circ$ ,  $21.05^\circ$ ,  $29.71^\circ$ ,  $43.57^\circ$ ,  $49.76^\circ$ ,  $56.73^\circ$ ,  $76.59^\circ$ ,  $85.19^\circ$  these peaks clearly indicate that potassium nitrate ions present inside the pore of nano-zeolite (Yildirim *et al.*, 2015).



**Figure 8. Methane emission ( $\text{mg m}^{-2} \text{day}^{-1}$ ) from the soil fertilized with  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$  Nano-Fertilizer to Rice (At 5% level p value =0.14 and SD-Error bar) Kinetics of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  release pattern**

The release of  $\text{NH}_4^+\text{-N}$  from nano-zeolite at the initial stage was very fast up to 10 Days and then the release was very slow but in control ( $\text{NH}_4$ )<sub>2</sub>SO<sub>4</sub> the release was very slow from the initial stage up to 13 days and then it became stable. The result clearly demonstrates that the nano-zeolite influence the slow release of  $\text{NH}_4^+\text{-N}$  ions (Fig. 5).



**Figure 9. The slow and steady release of N assisted in the reduction of nitrous oxide emission by 50% in nano-fertilizer fertilized soils**

The nitrate release pattern of nano-fertilizer showed that at the start of the experiment, the  $\text{NO}_3^-\text{N}$  was the highest concentration of  $105 \text{ mmol}^{-1} \text{N}$  in the leachate from nano-zeolite followed by potassium nitrate  $\text{mmol}^{-1}$ . Furthermore, it can be seen that at the initial stage, nitrate release from nano-zeolite occurred rapidly and after 10 days slow release was

detected. However, in control, the release was up to 12 days and thereafter it was stable (Fig. 6).

### Greenhouse Gas (GHG) emission

The nitrous oxide emission was measured at 30 and 60 DAT in rice soils exposed to various fertilization treatments. During the active tillering, plots applied with  $\text{NH}_4^+\text{-N}$  loaded nano-zeolite showed the lowest  $\text{N}_2\text{O}$  emission of  $0.88 \text{ mg m}^{-2} \text{day}^{-1}$  while the conventional fertilization practice registered the highest value ( $1.67 \text{ mg m}^{-2} \text{day}^{-1}$ ) which is nearly twice as that of treated plots. A similar trend of response was seen at 60 DAT (Fig. 7).

The p-value of the graph (Fig-7) shows that 0.035 at 5% level of significance, this value clearly proved that against null-hypothesis. The decrease in nitrous oxide emission through loaded zeolite in the rice field might be due to its honeycomb structure which possesses large cavities essential for maximum adsorption of  $\text{N}_2\text{O}$ . (Svelleet *et al.*, 2007) The  $\text{CH}_4$  emission was measured at 30 and 60 DAT in rice soils being exposed to various fertilization treatments. During the active tillering, plots applied with  $\text{NO}_3^-\text{N}$  loaded nano-zeolite showed the  $\text{CH}_4$  emission of  $13.6 \text{ mg m}^{-2} \text{day}^{-1}$  while the conventional fertilization practice registered the highest value ( $14.5 \text{ mg m}^{-2} \text{day}^{-1}$ ). A similar trend of response was seen at 60 DAT (Fig. 8). The p-value of the graph (Fig-8 shows that 0.14 at 5% level of significance, this value clearly fails to prove that against null-hypothesis. The results indicate there is no significant difference between control and treated plots in methane emission

### CONCLUSION

Overall, the results indicated that nano-fertilizer has the potential to regulate the release of N for an extended period (20 days) in comparison to the conventional urea fertilizer (9 days). The slow and steady release of N assisted in the reduction of nitrous oxide emission by 50% in nano-fertilizer fertilized soils in comparison to conventional fertilizer applied soils (Fig-9). There was a slight reduction in methane emission from the nano-fertilizer applied soils. More studies are required to validate the data obtained from the greenhouse experiment.

### ACKNOWLEDGEMENTS

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