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Full Length Research Paper

Manufacture and categorization of nanoporous zeolite based N fertilizer

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A laboratory study was undertaken to improve the nitrogen (N) use efficiency of urea using microporous natural zeolite (Z) and nanoporous zeolite (NZ) as substrate. The fertilizer composite was prepared under ambient conditions by impregnation urea in adsorbents. Z and nanoporous-zeolite measuring a dimension of 794, 87 nm were used for this study. The commercial urea fertilizer and adsorbents were blended or fused at varying w/w ratios of 1:1 to 1:10 using simple liquid immersion with hydrothermal technique. The 1:1 ratio of natural zeolite: urea and NZ: urea registered the highest total N content of 18.5 and 28%, respectively. The adsorbents and fabricated fertilizers such as zeourea (ZU) and nano-zeourea (NZU) of 1: 1 ratios were characterized using particle size analyzer, zeta potential, X-ray diffraction, FT-IR, Raman spectroscopy, and SEM with EDS besides release pattern of N. The data revealed that, the N release from the urea blended with NZ (1:1) was up to 48 days while the conventional Z - urea (1:1) mix was up to 34 day and the N release ceased to exist in urea within 4 days under ambient conditions. This suggests that, nanoporous zeolite based on N fertilizer (NZU) can be used as alternate strategy to improve the N use efficiency in crop production systems.

Key words: Nanoporous zeolite, Natural zeolite, Nano-fertilizers, Nitrogen, Slow release N fertilizers.

INTRODUCTION

Despite the fact that the atmosphere carries 78% of Nitrogen (N) and the soil organic matter possesses 98% N, still available N status of more than 90% of the arable soils are found deficient. Such low N status is attributed to the losses of N due to high rate of mineralization, volatilization, leaching, and denitrification. To prevent the problems arising from the high solubility of many N fertilizers and their potential vulnerability to leaching, especially in the nitrate form, a range of slow-release fertilizers (SRFs) and controlled-release fertilizers (CRFs) have been developed (Shaviv, 2000; Subramanian and Tarafdar, 2011). N should be continuously available throughout the growing season to provide optimum yield and quality. To develop N fertilizers with controlled release characteristics, the adsorbents zeolite, halloysite, montmorillonite, and bentonite nanoclays were used (Sharmila, 2010) and the purification of nanoclay is time consuming and costly affair excluded zeolite (Rs.12/- per kg). Zeolite pores can hold N much higher than other nanoclay. The present study is one of the pioneer

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Abbreviations: Z, natural zeolite, **NZ,** nanoporous, **ZU,** zeolite zeourea, **NZU,** nano-zeourea.

works to reduce the soil and water pollution by improving nutrient use efficiency (NUE).

Zeolites are abundant in nature and occurring along with low grade metamorphic rocks of hydrous alumina silicate mineral. They are a series of microporous ordered crystals with complex pores and are microporous, mesoporous, and nanoporous. Ions can be immobilized on zeolites by two mechanisms viz., ion exchange and chemisorption. Weak and strong chemical bond creation between ions and zeolite plays a major role of nutrient release and availability in soil solution. Natural zeolite (Z) and nanoporous zeolite (NZ) consists approximately 30 to 40% of channels of 0.4 to 1 nm pore diameter. This porespace (35 to 40%) would be used for loading N and Potassium (k) (Bansiwal et al., 2006). Utilizing preferential ion exchange property of zeolite helps to reduce and avoid the contamination of natural resources (Wei et al., 2011). Mesoporosity, nanoporosity and high surface area can be used for loading nutrients and it can be used as a slow release and novel nano-fertilizer.

The dominant process in N adsorption on these zeolites is influenced by the electric field created by the charge-balancing cations in the pores and by hydrogen-bonding with surface. In the recent years, NZ have attracted considerable attention due to the expectation of their unique surface properties, shorter diffusion pathlengths and higher cation exchange capacity (CEC) (Ramesh et al., 2010). Assessment of micro and nano-scale level of urea interactions with Z and NZ will provide valuable information about adsorption property, which will indirectly help in improving nutrient use efficiency and reduces loss of nutrients. Z has capacity to trap ammonia and retains N in the rooting zone of plants. The simplest method to impregnate N is to physically mix the urea in solution with the adsorbents support under given temperature, stirring and time conditions, followed by solvent removal by evaporation or filtration (Chang, 1997). Nano-fertilizers and nano composites can be used to control the release of nutrients from the fertilizer granules so as to improve the nutrient use efficiency while preventing the fixation or loss of nutrients to the environment (Chang, 1997). The present study hypothesize that, N derived from urea fortified in zeolite adsorbent facilitates slow and regulated release of N that may serve as a strategy to evolve slow release fertilizer with improved use efficiency.

MATERIALS AND METHODS

Fabrication of nanoporous zeolite based N fertilizer

A laboratory experiment was conducted to fabricate N fertilizers using Z and NZ and study the nutrient release pattern at the Tamil Nadu Agricultural University, Coimbatore during 2012. Z (clinoptilolite) was purchased from GM Chemicals, Ahmedabad and was used for this study. The Z or NZ based fertilizers were fabricated under ambient conditions by impregnation and simple liquid immersion hydrothermal technique (Chang, 1997).

Adsorbents Z and NZ were preheated (150°C for 3 days) in a hot air oven for efficient adsorption of N. Required amount of urea crystals were mixed with distilled water by weight and continuous shaking. The urea solution was heated at 115°C till it changed from the crystal structure to liquid and then the required quantity of adsorbents (Z or NZ) were added at different ratios of 1:1, 1:2, 1:3, 1:5, and 1:10 on w/w basis. The prepared mixer was heated continuously till the liquid fertilizer is completely absorbed on the Z or NZ. Cooling down the mixer with air (80ºC) and it gives to crystal structure and it became a solid inside. Constant cooling (50ºC) of solid material and add polymer (carboxyl methyl cellulose sodium salt) with continuous mixing (approximately 10% of the weight of the Z or NZ). The polymer reduces contact and release nutrient as slow. Air dried the mixture and powdered for further study. Ten different range of fertilizers of urea loaded Z and NZ (1:1, 1:2, 1:3, 1:5, and 1:10) were prepared with continuous shaking. The total N content of fabricated fertilizers was estimated (Muthuvel and Udayasoorian, 1999). Detailed physio-chemical properties of Z and NZ were given (Table 1).

Characterisation

The adsorbent (Z, NZ) and fabricated fertilizers (ZU, NZU) were characterized using particle size analyser (PSA), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), Raman Spectroscopy,Scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDS) estimated as per standard procedure (Das and Ansari 2009).

Particle size distributions and Zeta potential measurements

Both adsorbents (Z, NZ) and fertilizers (ZU, NZU) were sieved through 40 µm sieves and the particle sizes were measured using PSA (Horiba Scientific Nanopartica SZ-100). About 0.5 mg of sample was dispersed in 20 ml of water and sonicated for 30 min with 10 seconds on-off cycle. The samples were dispersed and a drop of 0.02% Tween-80 was added in water. The size measurements were performed at 25°C at 90º/173º scattering angle.

X-ray diffraction patterns

The X-ray diffractograms have been recorded on Powder XRD (Bruker D8 Advance Powder X-ray Diffractometer, Germany). The machine exploits Cu-Kα radiation (0.154 nm) for measuring the crystalline nature of atoms in the material (Toraya, 1986). The diffractograms were recorded in the range of 2θ = 10-80 degrees at a scanning speed of 0.080 and step times 1s at room temperature 25ºC.

FT-IR spectra and raman shifts

The adsorbents and fertilizers were finely ground and mixed with KBr to 0.1% and then pressed into pellets prior to measure the IR spectra (Byler et al., 1991). Each pellet of the sample weighed approximately 2 mg. The spectra of the samples were determined at 2 cm^{-1} resolution, 0.44s/scan on a using Shimadzu Model-FTIR. Raman Shifts were measured in powdered adsorbents and fertilizers using Raman Spectroscopy (R-3000 QE TM). The laser wavelength was 785 nm produced by a diode solid state laser operated at 100 mW at the source (Frost, 1997). The machine was set in the spectral range of 200 to 2000 cm^{-1}. All graph were prepared using Microcal origin 6.0 software.

Table 1. Physio-chemical properties of natural zeolite and nanoporous zeolite.

Property	Natural zeolite	Nanoporous zeolite
pH (1: 6.25ml ratio)	9.6	8.14
EC_e (dSm^{-1}) (saturated paste)	0.17	0.06
Moisture (%)	10	12
Bulk density (Mg m^{-3})	0.57	0.50
Particle density (Mg m^{-3})	0.66	0.39
Pore space (%)	34	45
Total organic carbon (%)	1.9	1.03
Total nitrogen (%)	0.02	0.03
Total phosphorus (%)	0.06	0.02
Total potassium (%)	0.09	0.02
Calcium* (%)	5.25	-
Magnesium* (%)	6.03	-
Silica* (%)	4.78	1.49
Aluminium* (%)	1.02	1.59
CEC(cmol(p^+) Kg^{-1})	100	106
Inorganic carbon (%)	28	45

*EDS data

Scanning electron microscope (SEM) with EDS

Surface morphology and cross sectional analysis was conducted using SEM (FEI Quanta 250). The samples were prepared onto adhesive carbon tape on an Aluminum stub. Varying magnifications were used to compare the structure and surface characteristics of the zeolite. The images were taken at an accelerating voltage of 20 kV. Surface element analysis was also conducted simultaneously with the SEM at the same surface locations using EDS. The EDS can provide rapid quantitative with adequate standards, semi-quantitative analysis of elemental composition with a sampling of 1 to2 µm.

Nutrient Release Pattern

To study nutrient release pattern, the percolation reactor was designed (Bansiwal et al., 2006). The reactor consisted of a glass cylinder (internal diameter = 2.5 cm, height = 15 cm) with 4 pore holes and experiment was conducted under ambient temperature. 10 g of soil was homogenised with adsorbents (Z, NZ) and fertilizers (ZU, NZU and Urea alone) which comprised 6 treatments along with control (soil alone). The 50 ml of deionized ultrapure water was added to the above from 1 to 50 days. Solutions were collected to determine ammonium and nitrate ions as per water quality standard protocol (Tandon, 1993). By this technique, comparative study of slow release tendency for adsorbents and fertilizers would be estimated, to develop a novel fertilizer.

Statistical analysis

All triplicate data were analysed using the analysis of variance (ANOVA). The Student's t-test was used with statistical significance for all tests were considered as $P < 0.05$.

RESULTS AND DISCUSSION

Nitrogen content of fertilizers

The total N contents of the urea alone (46%), fertilizer mixtures of urea and Z ratio at 1:1, 1:2, 1:3, 1:5, 1:10 were 18.5, 11.5, 9.0, 4.2, and 0.5% (Figure 1). While the same set of fertilizer mixture ratios with NZ, the total N content increased to 28.0, 26.3, 13.5, 5.0 and 0.7%, respectively. The data clearly indicated that, the N contents of NZ based fertilizer mixture were consistently higher regardless of urea: Z ratios. The highest N content of 28.0% was recorded in 1:1 ratio (urea: NZ) which was significantly higher than conventional urea: Z mixture at the same ratio (18.5%).

The data suggest that, the size reduction in adsorbent (natural zeolite) from micro to nano-dimension coincided with an increase in N content by 33.3%. Such phenomenal increase may be attributed to the extensive surface area exhibited by nano-based formulations that facilitates adsorption processes. The results are in conformity with the observations of reported literatures by Chang (1997), Behnassi et al. (2011) and Kerr (1986) on nano-mediated nutrient release from smart customized fertilizers. It is well understood that, the unique property of nanotechnology is the high surface - mass ratio. Z possesses a surface of 648 m^2 g^{-1} while the same zeolite in nano-dimension measures 1126 m^2 g^{-1}. Thus, the extensive surface area would have helped the NZ to retain N which reflected on the N content of the fertilizer formulation (Taufiqurrahmi et al., 2011) and NZ with urea solution complex reduce the urea hydrolysis rate (Komarneni, 2009; Wang et al., 2010).

Characterisation

The results on particle size distribution (PSD) with zeta potential of adsorbents (Z, NZ) and fertilizer formulations of 1:1 ratio (ZU, NZU) are given (Table 2). The mean

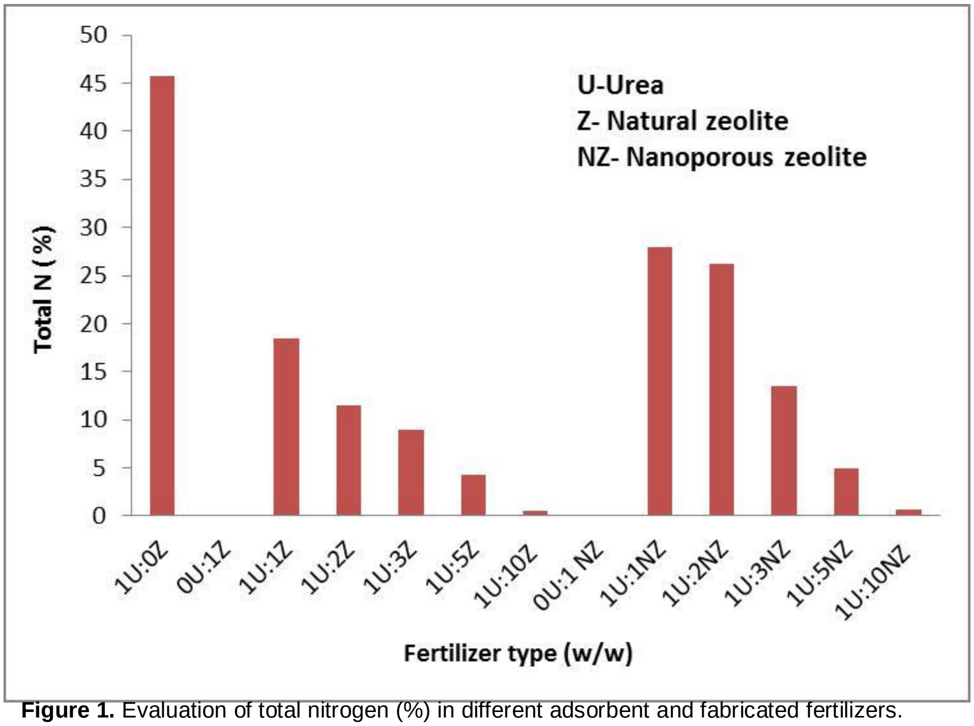


Figure 1. Evaluation of total nitrogen (%) in different adsorbent and fabricated fertilizers.

Table 2. Average particle size distribution (PSD), zeta potential of natural zeolite, nanoporous zeolite and fertilizer formulations at 1:1 ratio.

Source	PSD (nm)	Zeta potential (mV)
Natural zeolite (Z)	794	-45.9
Zeourea (ZU) (1:1)	1120	-49.4
Nanoporous zeolite (NZ)	87	-50.4
Nano-zeourea (NZU)(1:1)	366	-64.3

data on PSD indicated that, particle sizes of micro-zeolite (1120) and NZ (87) had increased when N is impregnated into the adsorbent of 1:1 ratio 1120 and 366 nm respectively (Figure 2). The results are in agreement with an observation which has suggested the reduction size of zeolite from 1000 nm to 3040 nm on high energy ball milling for more than 6 h (Sharmila, 2010). This top down approach has facilitated extensive surface area for adsorption of cationic nutrients and anionic nutrients on surface modification of the zeolite with cationic surfactant. Our study has clearly shown that the zeta potentials of the particles in the range of -30 to -65 indicating the stability (Figure 3). The Zeta potential indicates the stability of sample and minimal aggregation of fabricated fertilizers.

The XRD patterns of the sample showed the maxima at 2θ = 30.8, 22.30, 26.64, and 22.32 for zeolite alone, zeourea (1:1), NZ alone, and nano-zeourea (1:1) that corresponded to *d* spacing = 2.89, 3.97, 3.33, and 3.96 Aº respectively (Figure 4a to d). On comparing the data of adsorbents and fabricated fertilizers with those of loaded N, it is observed that, they closely resemble with each other, indicating that the structural integrity of material is retained after loading of N (Toraya, 1986).

The FT-IR spectrum of finely ground naturally occurring natural zeolite, zeourea, NZ, and nanozeourea has shown the functional groups (Figure 5a to d) and were studied. Zeourea yielded the spectra of 817 for nitrate ion, 1242 for C-N and 1512, 1651 cm^{-1}for N-H strectching bands. Nano-zeourea yielded the spectra of 1288 for C-N and 1512, 1561cm^{-1} for N-H strectching bands. Samples were triggered for molecular vibrations through irradiation with infrared light and provide mostly information about the presence or absence of certain functional groups (Byler et al., 1991).

The data on Raman shift measured for adsorbents and fertilizers are given Figure 6a to d. The broad signal collected at 1125 and1108 cm^{-1} for zeolite and NZ, respectively. The Raman spectra in the fertilizer formulations such zeourea and nano-zeourea had a

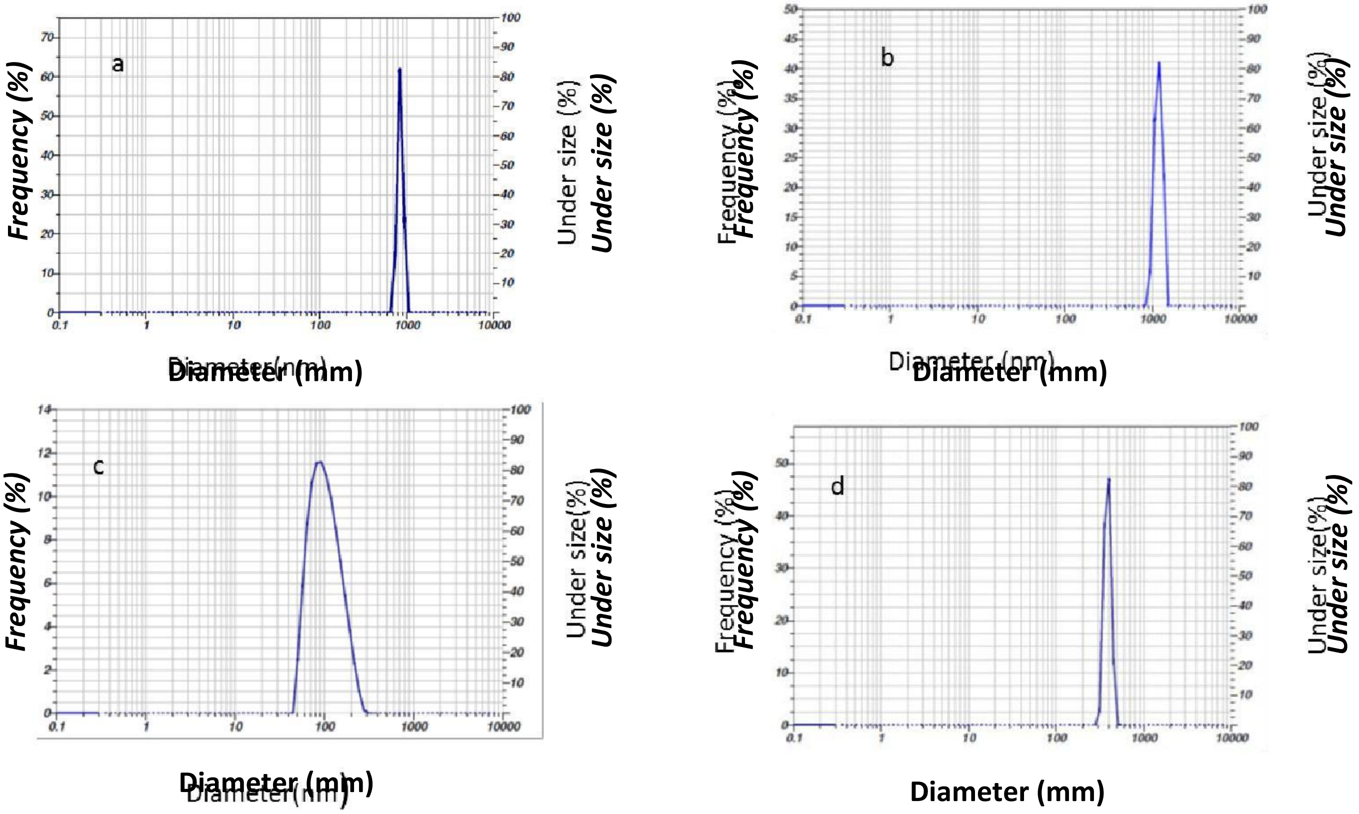


Figure 2. Particle size distributions (nm) of (a) Natural zeolite, (b) Zeourea, (1:1) (c) Nanoporous zeolite, (d) Nano-zeourea (1:1).

change in the magnitude of signal at 1114 and 1008 cm^{-1} indicating N on adsorbents (Frost, 1997; Peter et al., 2011). The intensity of the Raman signal decreases as particle size increases.

The surface morphology of NZ and nano-zeourea (1:1) was examined by SEM (Figure 7a to b). The N loading had changed the shapes and geometry of NZ from the sharp edges to the rounded besides aggregation of NZ. The EDS elemental analysis has estimated the silica and aluminium element ratios for NZ and nano-zeourea as 9.25/10.31 and 2.29/2.39, respectively (Figure 7a to b). Further, EDS quantified N content NZ and nano-zeo urea as 1.14 and 31.2%, respectively. The data clearly showed that, N has been successfully loaded into the adsorptive sites of NZ. The results are in conformity with the earlier observations (Sharmila, 2010; Ramesh et al., 2010; Komarneni, 2009) which have suggested size reduction of zeolite facilitates adsorption of NH_4 ions that is derived from the hydrolysis of urea.

Percolation reactor study

The release of NH_4^+-N and NO_3^- - N from adsorbents and fabricated fertilizers are presented in Figures 8 and 9). The data illustrated that, the NH_4^+-N release from urea, zeolite + urea (1:1), NZ: urea (1:1), zeourea, and nano-zeourea were 65, 45, 37, 21, and 18%, respectively, in the fertilizer formulations detected on the first day of the experiment (data not shown). Similar observations were reported earlier (Subramanian and Tarafdar, 2011; Ramesh et al., 2010). The first day of leachate solutions had 2716, 3486, 3346, 2758, and 2587 mg L^{-1} of NH_4^+-N and 490, 378, 280, 98, 126 mg l^{-1} of NO_3^- - N in urea, zeolite + urea (1:1), NZ: urea (1:1), zeo-urea and nano-zeourea, respectively.

The release of N from urea (irrespective of NH_4^+-N and NO_3^- - N) ceased to exist within 4 days of the experiment. The same set of treatments showed N release for 4, 13, 20, 34, and 48 days, respectively. This data strongly suggested that, NZ is a potential adsorbent to regulate the release of N. The percolation reactor study clearly demonstrated that, size reduction of the adsorbent assists in extensive surface area for N adsorption or desorption. Our data corroborated with the results of other published reports (Gholizadeh, 2008; Gioacchini et al., 2006; Zhang et al., 2006; Komarneni, 2009).

Conclusion

We made an attempt to improve the N use efficiency using NZ as an adsorbent. The N use efficiency of conventional urea hardly exceeds 30 to 35% and NZ has

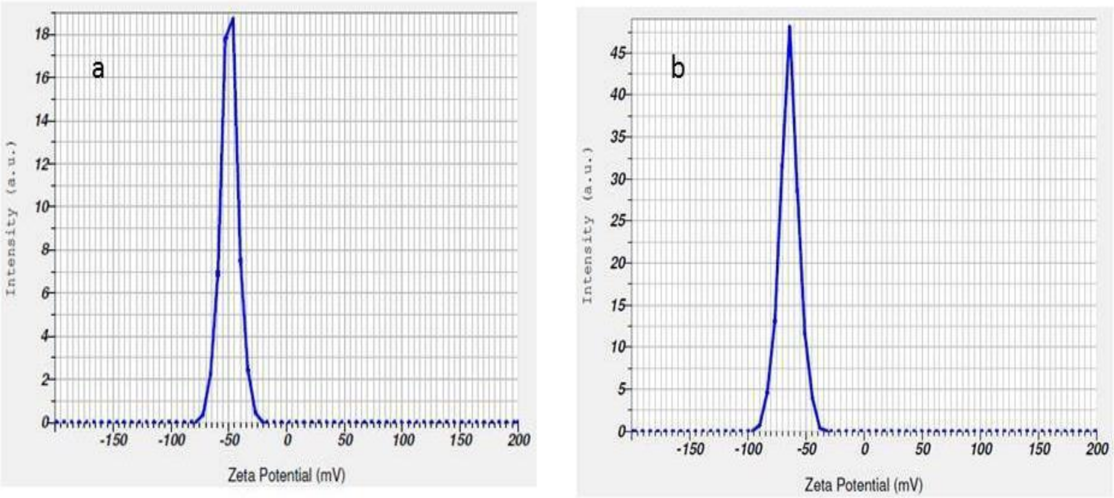


Figure 3. Zeta Potentials (mV) of (a) Zeourea (1:1), (b) Nano-zeourea (1:1).

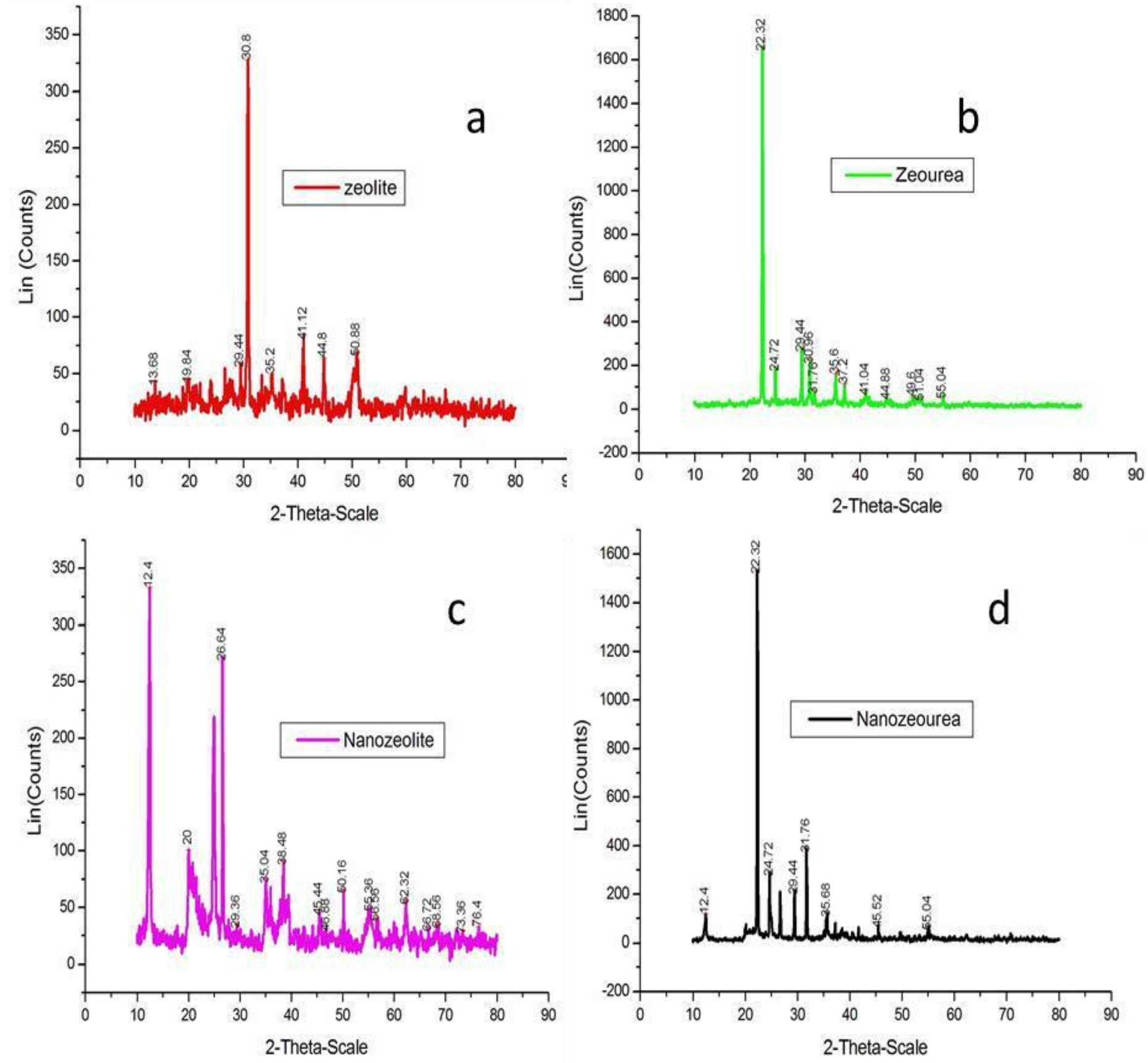


Figure 4. Powder X-ray diffraction patterns (Aº) of (a) natural zeolite, (b) zeourea (1:1), (c) nanoporous zeolite, (d) nano-zeourea (1:1).

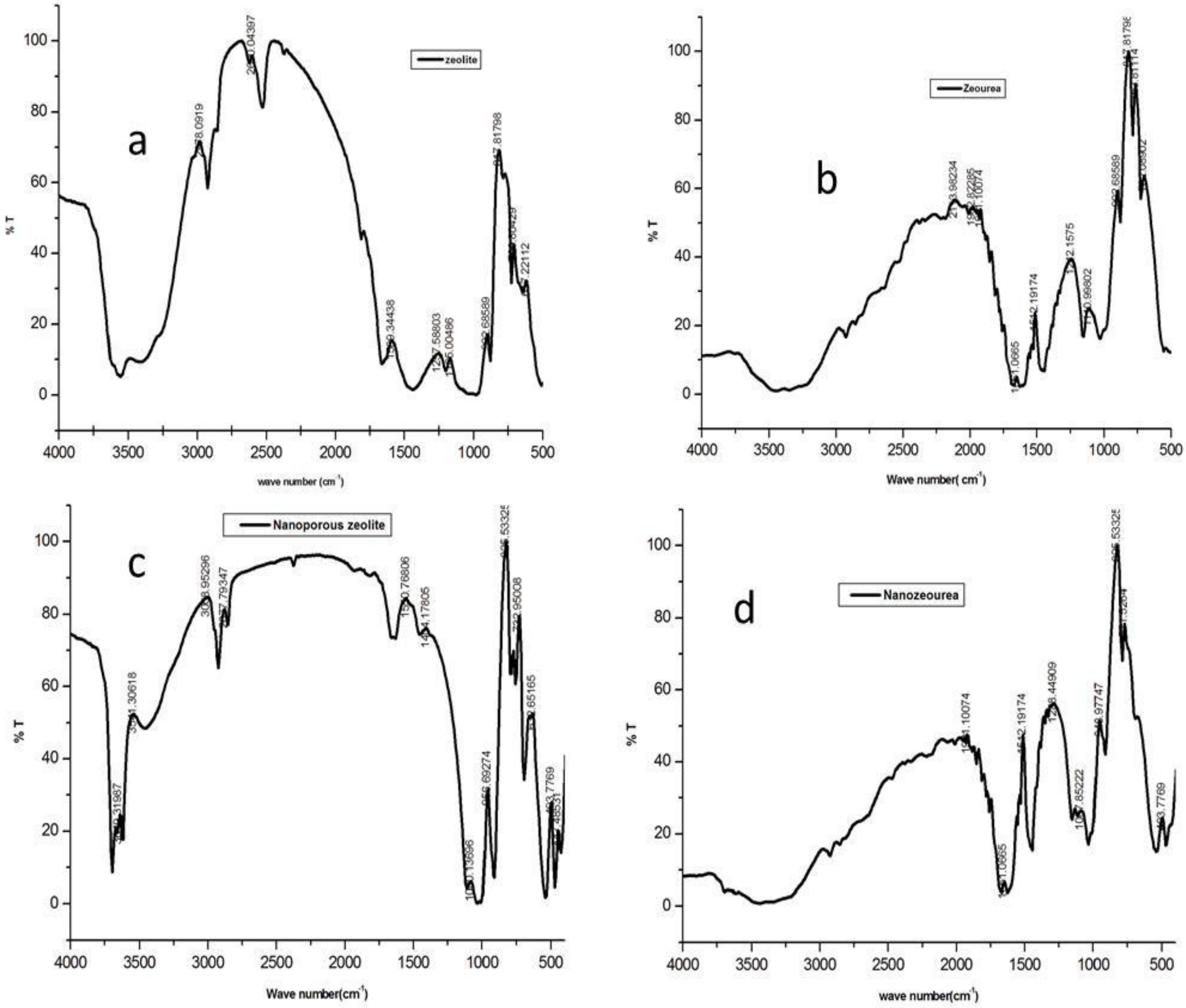


Figure 5. FT-IR spectra (cm^{-1}) of (a) natural zeolite, (b) zeourea (1:1), (c) nanoporous zeolite,, (d) Nano-zeourea (1:1).

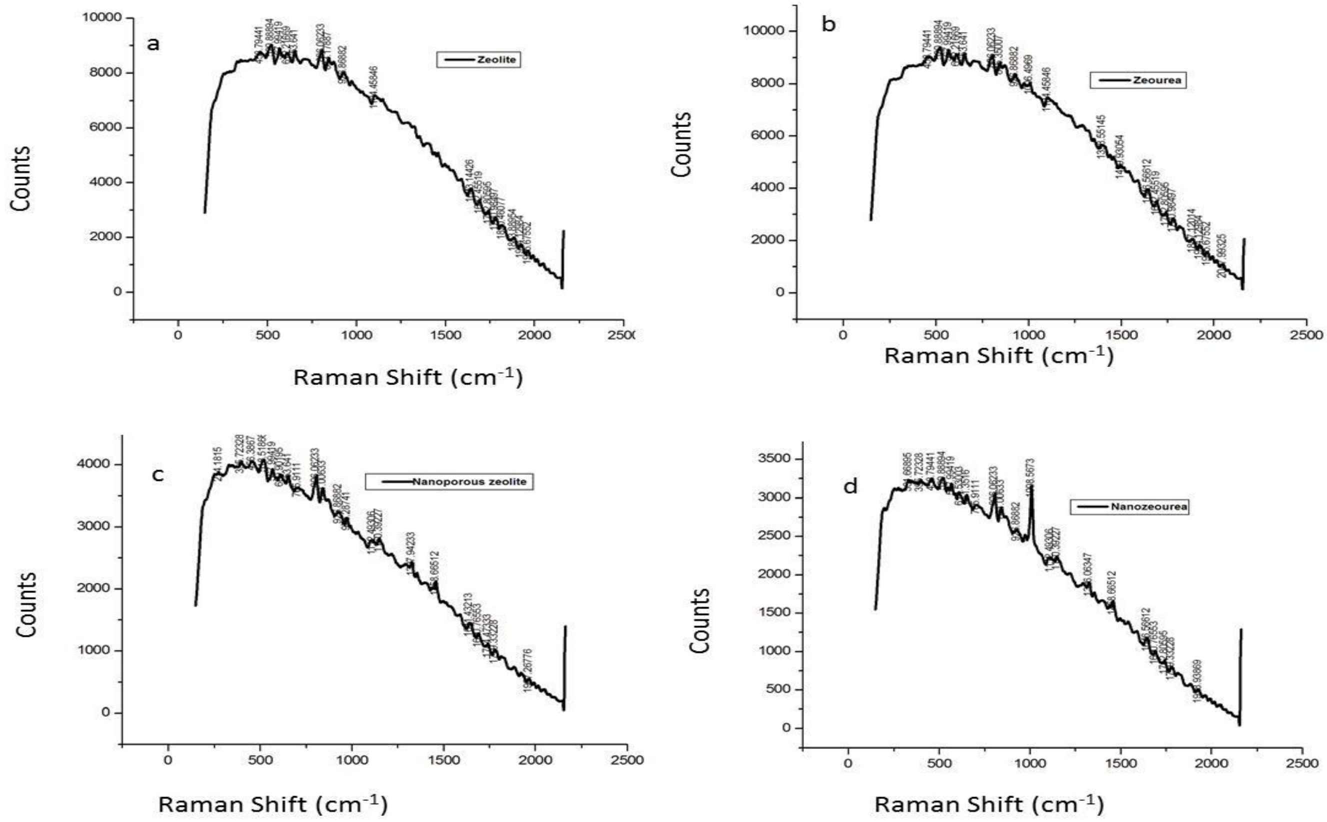
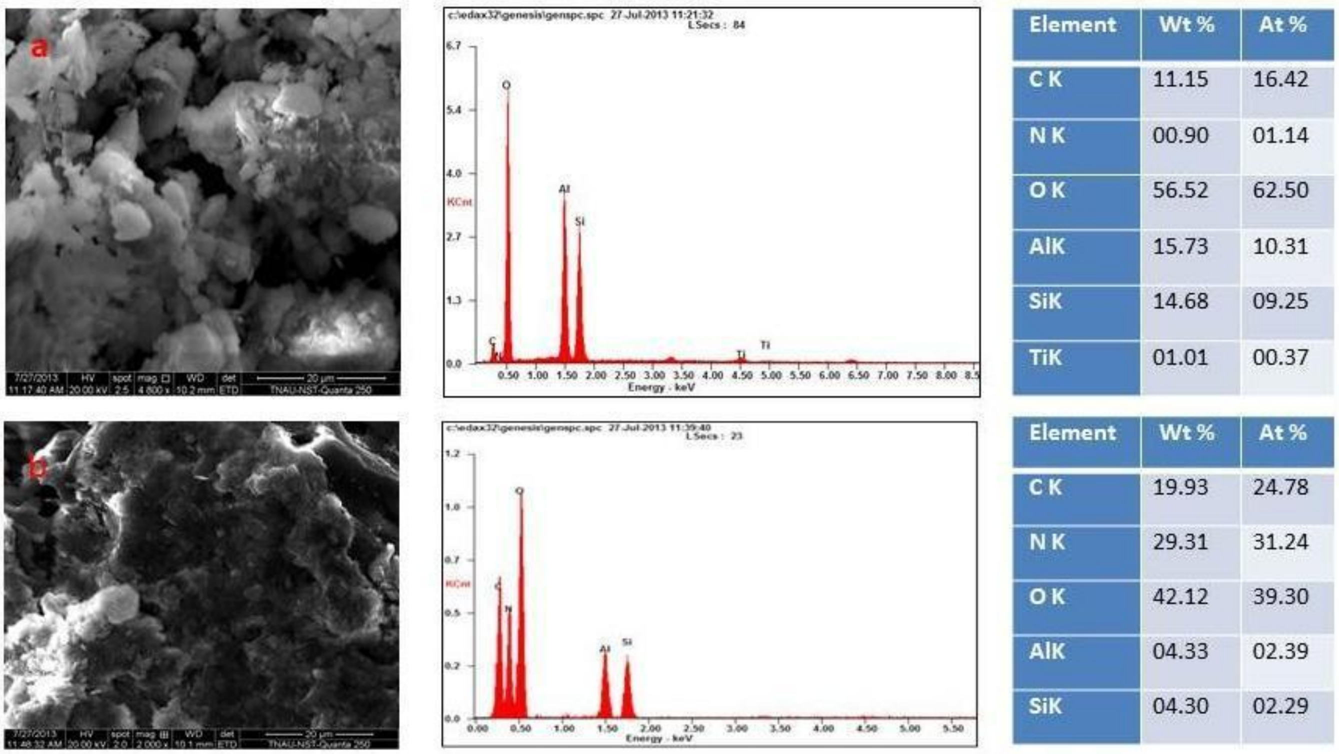


Figure 6. Raman Shift (cm^{-1}) of (a) natural zeolite, (b) neourea (1:1), (c) nanoporous zeolite, (d) Nano-zeourea (1:1).



Element	Wt %	At %
C K	11.15	16.42
N K	00.90	01.14
O K	56.52	62.50
AlK	15.73	10.31
SiK	14.68	09.25
TiK	01.01	00.37

Element	Wt %	At %
C K	19.93	24.78
N K	29.31	31.24
O K	42.12	39.30
AlK	04.33	02.39
SiK	04.30	02.29

Figure 7. SEM micrograms with EDS of (a) nanoporous zeolite, (b) nano-zeourea (1:1).

enormous potential to regulate the release of N thereby fertilizer use efficiency can be improved. NZ fortified urea facilitates adsorption of N in channels and porespaces. The zeourea and and nano-zeourea contained 18.5 and 28% of N and capable of releasing N up to 34 and 48 days, respectively, while the N release from conventional urea is just 4 days. The data strongly suggested that, zeolite with nano-dimension can help to improve N use efficiency besides sustained release of N that may considerably economize the N use in crops with an added advantage of prevention of groundwater contamination.

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