

## Ball milled nanosized zeolite loaded with zinc sulfate: A putative slow release Zn fertilizer

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### ABSTRACT

Commercially available zeolite was ball milled and the resultant nano sized product was characterized with powder XRD, SEM, FT-IR and BET. Ball milled nano-sized zeolite was mixed with zinc sulfate solution at various concentrations. Zinc sorption and desorption studies were carried out. Nano zeolite loaded with zinc sulfate showed the highest sorption among native and ball milled zeolite and montmorillonite, halloysite and bentonite. The results showed that the highest sorption of 429.5 mg kg<sup>-1</sup> was observed for nano-zeolite with highest bonding energy ( $0.33 \text{ mmol}^{-1} \times 10^{-3}$ ) and regression coefficient (0.99). The nano-zeolite recorded 47.9% higher adsorption than nano-montmorillonite. Nano-zeolite showed the release of zinc in three stages. Zn levels decreased sharply in the first 220 hours ( $k_1 = 0.53$ ), and stabilized thereafter. The result also showed that from 300 to 500 hours it follows second stage ( $k_2 = 9.44 \times 10^{-3}$ ). In this stage it supplies 2 ppm of Zn<sup>2+</sup>. The next stage falls from 500 hours ( $k_3 = 1.7 \times 10^{-3}$ ) and it supplies 1.5 ppm of Zn<sup>2+</sup> and this condition is static even after 1000 hours. This study suggests that nano-zeolite based Zn fertilizers may be used as a strategy to achieve the slow release of Zn which in turn would improve Zn use efficiency in crops.

**Key words:** Nano-zeolite, percolation reactor, slow release fertilizer, agriculture, horticulture

### INTRODUCTION

Nanotechnology is a highly promising technology that spans many areas of science and technological applications. Rapid advancements in nano sciences and nanotechnologies in recent years have opened up new horizons for agriculture and allied sectors (Adebowale *et al.*, 2005) There are several slow release nitrogenous fertilizers such as neem coated, gypsum coated or tar coated urea to improve the N use efficiency. But the fertilizers vanished at the commercial stage due to the non-availability or practical field problems associated with it. There are no slow release Zn fertilizers available in the market and this is one of the first attempts to look at the slow release pattern of Zn<sup>2+</sup> as a result of use of nano-carriers such as zeolite.

Zinc is one of the essential micronutrients required for optimum crop growth. Plants take up zinc in its divalent form (Zn<sup>2+</sup>). Zinc plays an important role in many biochemical reactions within the plants (Ali and Abidin, 2006). Both field crops (maize and sorghum and sugarcane) and horticultural crops (fruits and vegetables) showed reduced photosynthetic carbon metabolism due to zinc deficiency (Almaraz Veronica *et al.*, 2003). Zinc modifies and/or regulates the activity of carbonic anhydrase, an enzyme that regulates the conversion of carbon dioxide to reactive bicarbonate species for fixation to carbohydrates in these plants (Amer *et al.*, 2010). Zinc is

also a part of several other enzymes such as superoxide dismutase and catalase, which prevents oxidative stress in plant cells (Antonyuk *et al.*, 2008). Zeolites are crystalline aluminosilicate minerals of the alkali and alkaline group elements and have a molecular sieve action due to their open channel network, thereby allowing some ions to pass through while blocking others (Bansiwal *et al.*, 2006, Broadley *et al.*, 2007) All zeolite framework structures have a three dimensional arrangement of TO<sub>4</sub> tetrahedra (T= tetrahedrally co-ordinated atom, usually Si<sup>4+</sup>, Al<sup>3+</sup>). These tetrahedra are linked together by the sharing of oxygen atoms and result in an open and stable three dimensional honeycomb structure with an overall negative charge, which is balanced by the cations that move freely in and out of its framework. Ion exchange is an intrinsic property of most zeolites. The cation exchange capacity of a zeolite is a consequence of the degree of substitution of Al<sup>3+</sup> for Si<sup>4+</sup> in the framework. These charge balancing cations are generally exchangeable, and channel structure of zeolites is responsible for their function as a “molecular sieve”. The channels and cages of a particular zeolite are clearly defined in their dimensions and shape, owing to high crystalline structure of these materials. The open channels thereby allow ions to pass through very freely. On the other hand, it is possible for ions to exchange only partially, because the volumes of the ions are such that these completely fill the intra crystalline space in the channels before 100% exchange is attained

(Chirenje, *et al.*, 2005). Thus, zeolite may show great promise as anion and cation carriers for CRFs to control zinc release. It is hypothesized that nano zeolite are negatively charged and they are capable of adsorbing  $Zn^{2+}$  ions that facilitate slow steady and regulated release of nutrients. This process will result in nano-fertilizer formulations that assist to regulated release of nutrients and improve zinc use efficiency while preventing environmental hazard.

## MATERIALS AND METHODS

### Synthesis of zeolite based nano-fertilizer

The zeolite (clinoptilolites) (GM Chemicals, Ahmedabad, India) were of vulcanoclastic origin, with a high cationic interchange capacity [ $270\text{ C mol (p}^+) \text{ kg}^{-1}$ ]. The clinoptilolite was subjected to ball milling to achieve particles of 30 nm in diameter. Commonly occurring nano-clays such as halloysite, montmorillonite, and bentonite of 30-40 nm sized particles (Sigma Aldrich chemicals, Bangalore) were used for the study. The physico chemical properties of zeolite and nano-were estimated following standard protocols (Cichocki, 2001).

### Particle size analysis

The samples were analyzed for size using DELSA Nano Particle Size Analyzer (Beckman Coulter Counter, Model ZM, Beckman Instruments, Fullerton, CA). All samples were dispersed in deionized water. The sample was sonicated using Sonicator (Model MS-50, Heat Systems, UItrasonics, Inc., USA) for five minutes at 1500rpm before the average particle size measurement was done.

### Shape

The Scanning Electron Microscopy (FEI, Quanta 200, Phillips, Netherlands) was used to get the shape of the nano-clays. About 0.5 to 1.0 g of nano-clay sample was dusted on the carbon conducting tape. Then the tape was mounted on sample stage and the images were taken in 16,000

magnification and 12.50KV.

### Surface Area measurement

X-Ray Diffraction technique was used for rapid surface area determination. Approximately one gram of samples was dusted on a glass substrate. Care should be taken that the surface on the glass substrate should be even and it was mounted on the sample stage and diffraction was measured. From this an automatic strip chart record of the sample peak was obtained. The well known Deby-Scherrer formula provides the relationship between mean crystallite size and diffraction line breadth.

### Bulk Density

The bulk density, particle density were determined by cylinder method as given by (Gupta and Dhakshinamurthi, 1980). Exactly 20 g of nano-clay samples were taken and transferred to 100 ml measuring cylinder and compacted by tapping 20 times and the volume was noted. Then 50 ml of water was added along the sides of the cylinder using pipette till the entire mass was completely soaked. The cylinder with nano-clays and water kept in an undisturbed condition for at least 30 minutes so that the entire pore space was completely filled with water. The final volume of soil plus water after the expiry of time and the bulk density was calculated.

### Colour

Munsell colour chart is used for measuring the colour. The colour of the dried powder of nanoclay was determined by matching the clay samples with the colour chip. The colour chip which closely matches was taken as the colour.

### pH and Electrical Conductivity

The pH and Electrical Conductivity (EC) of the nano-clay samples was determined using pH meter and EC meter as per the procedure given by (Cichocki, 2001). Exactly 20g of nano-clay sample was taken into a clean 100 ml beaker.

**Table 1:** Physical and chemical properties of nano-zeolite and nano-clays

Parameters	Zeolite	Montmorillonite	Halloysite	Bentonite
Physical Properties				
Size (nm)	25-30	30-40	30-40	30-40
Shape	Cubical	Irregular Flakes	Tubular	Round
Surface Area ( $\text{m}^2 \text{g}^{-1}$ )	1300	1000	150	80
Bulk Density ( $\text{g cc}^{-1}$ )	0.30	0.46	0.35	0.90
Color	5Y 7/4	5Y 8/1	2.5Y 8/2	2.5Y 7/4
Chemical Properties				
pH of 1% slurry	7.9	8.0	8.2	10.4
EC ( $\text{dSm}^{-1}$ )	0.02	0.02	0.03	0.35
CEC ( $\text{C mol(p}^+) \text{ kg}^{-1}$ )	270	180	80	60
$\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio	1.95	1.83	1.72	1.65

Then 50 ml of distilled water was added. The content was stirred intermittently and allowed to stand for half an hour. After half an hour the meter reading was recorded.

### Cation Exchange Capacity of clays

The Cation Exchange Capacity (CEC) of the clays were determined using the complexes of copper (II) ion with Triethylenetetramine and tetraethylenepentamine (He, *et al.*, 2002). Two hundred mg of clay sample was added to 35 ml of distilled water. Water was added to make the final volume of 50 ml and transferred into a 100 ml beaker. While stirring the suspension, 10 ml 0.01 M copper(II) trien sulphate solution (1.463 g of triethylenetetramine were dissolved in 100 ml of distilled water) was added. Another solution was prepared by mixing 1.596 g of dry Cu(II) sulphate with distilled water. These solutions were mixed together and added. After 3 min reaction time, the suspension was centrifuged with a micro centrifuge at 13,000 rpm for 3 min. The supernatant solution was carefully removed and the intensity was measured at 620 nm in a 10 mm cuvette against water as a blank. The CEC was then calculated.

### Sesquioxide content

Sesquioxide of nano-clay was estimated based on the principle that iron and alumina are precipitated as their respective hydroxides by the addition of ammonia. Then they are converted into oxide forms by ignition and the residue was weighed. First, 50 ml of the HCl extract was pipetted out into a 250 ml beaker. Then 1 g of solid ammonium chloride was added and boiled. The beaker was removed from the flame and diluted ammonium hydroxide was added till the solution becomes alkaline. Again boiled for 4 to 5 minutes and filtered through Whatman No.42 filter paper. The residue was washed with hot water till the filtrate runs free of chloride. The precipitate on the filter paper was dried and transferred to a weighed silica crucible and the constant weight was recorded after ignition. The sesquioxide content was reported in percentage.

### Atomic Force Microscopy

Atomic force microscopy (AFM) is a method of measuring surface topography on a scale from angstroms to 100 microns. About 0.1 mg of nano-clays were dissolved in 1ml of acetone. In order to increase the adhesive properties of the mica substrate, poly D-lysine was spread on the surface. One drop of suspension was spread on the mica substrate and setting it aside for few minutes for drying. After drying, the substrate was mounted on sample stage and the images were taken under non tapping mode. The (AFM) images were obtained by means of a NanoScope III (Veeco Dimension 3100 AFM, Veeco Instruments, UK) apparatus using a non tapping mode.

### Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is a powerful tool for identifying types of chemical bonds in a molecule by producing an infrared absorption spectrum. Clay sample and IR transparent material like KBr was mixed in the ratio of 2:1 in a mortar and pestle for 30 minutes. Then the mixture was converted into pellets by pressing the prepared mixture with a hydraulic or hand press into a hard disk. The pellet, ideally 0.5 to 1 mm thick was then placed in a transmission holder and scanned. Typically, the pellet technique provides good quality spectra with a wide spectral range and no interfering absorbance bands. Then, the spectra was obtained by Hewlett Packyard Model 8452 A diode Array Spectrophotometer.

### Energy dispersive X-ray spectroscopy

Energy dispersive X-ray spectroscopy (EDAX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. (It was done by FEI Quanta 200 EDAX, Phillips, Netherlands).

### Surface Modification of nano-clays

Negative charges of the nano-clays were modified by treating them with a surfactant hexadecyltrimethylammonium bromide (HDTMABr) (M/s. Sigma Aldrich, Bangalore) as suggested by (Hernandez *et al.*, 1994). A pre-weighed quantity of nano-clays samples were mixed with HDTMABr solution in a 1:100 (solid: liquid) ratio. The solution was agitated for 7-8 h at 150 rpm in a centrifuge. The solution was then filtered, and the solid residue was washed with double-distilled water and air-dried for 4-6 h. The synthesized surface modified nano-clays (SMNC) were then mechanically ground with a mortar and pestle to a fine particle size.

### Zinc sorption

To study the sorption behavior of zinc on surface modified nano-clays, to each 40-ml centrifuge tube, 2.5 g of nano zeolite and 25 ml of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 M zinc sulphate solution were mixed for 24 h at 150 rpm. The mixtures were then centrifuged and the solution was filtered (Whatman no. 42 filter paper pre-washed to eliminate contamination) and zinc concentration was determined by Atomic Adsorption Spectrophotometer (Varian, AA 240, Varian, Inc., USA) The amount of zinc adsorbed was calculated from the difference between the initial and equilibrium solution concentrations. Then the data were fitted with Langumir equations (Jackson, 1973).

### Preparation of Slow Release Fertilizers

To each 250ml centrifuge tube, 60 g of nano-clay was

homogenized with 250 ml of 1 M zinc sulphate solution for 8 h and filtered, washed three times with deionized water, and air-dried. The solid:liquid ratio used was 1:10 for the synthesis of zinc loaded nano-clays (Hernandez, *et al.*, 1994).

### Soil

The soil samples collected from Maize Research Station, Vagarai, TNAU was used for this study to simulate the actual field conditions.

### Experimental Design for Nutrient Release

The chemical reactor designed for a constant flow of (Jakkula, 2005) solution in several studies concerning zeolites was used. Inside the reactor, 5 g of soil overlaid with the nano-zeolite loaded with zinc sulfate were placed. Solutions were collected to determine ammonium and nitrate ions. The mean temperature during the experiment was  $25 \pm 0.2^\circ\text{C}$ .

## RESULTS AND DISCUSSION

### Characterization of nano-clays

The nano-zeolite and other nano-clays (montmorillonite, halloysite and bentonite), after loading with  $\text{Zn}^{2+}$  were scanned through SEM to know the surface morphology (Fig. 1). It showed that the nano zeolite was typical cubic to round in shape. Surface morphology of nano-zeolite after attaching Zn ions (Fig.2) is in confirmation with the results obtained by Kim, *et al.*, 2004.

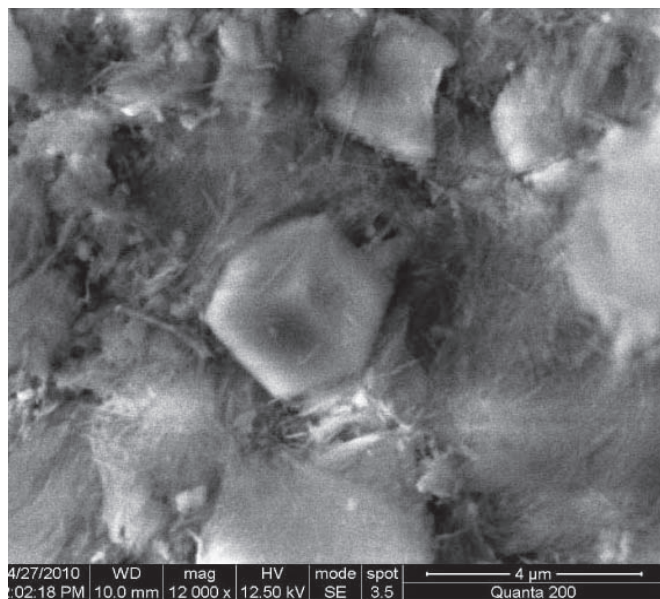


Fig. 1: Nano zeolite

The data were confirmed by the FTIR. IR spectra of unloaded nano-zeolite having the characteristic peak at 3618, 3440  $\text{cm}^{-1}$  (Fig. 4a). The IR pattern of nano zeolite loaded with Zn with the characteristic peaks at wave numbers 1643, 1404, and 840  $\text{cm}^{-1}$  (Fig. 4b). There was lot of differences in peaks after loading with Zn. There was shifting in peaks because of loading of Zn. Then it was compared with the reference peak (Fig. 4c). It showed that, the peak at 1503, 1331 and 833  $\text{cm}^{-1}$  for zinc in reference graph referred to Zn. The same range of peaks at 1331 and 833  $\text{cm}^{-1}$  was also obtained in Fig.1b which was nano-zeolite load with Zn which is in confirmation with the observations made by Langmuir, 1961.

The phase and 3D AFM images of nano-zeolite and nano-clays after loading with zinc are given in the Fig. 3a and 3b. The phase image of zinc loaded nano-zeolite showed the way in which the zinc ions were attached on the surface. Using software of AFM, from a typical horizontal line analysis, for nano-zeolite, we obtained the Roughness average (Ra) to be 1.53 nm, maximum height of the profile above the mean line (Rp) to be 12.56nm, mean of maximum height above mean line (Rpm) to be 7.32 nm, maximum peak to valley height (Rt) to be 18.36 nm and mean of peak to valley height (Rtm) to be 13.19 nm. Similar results were obtained by (Minceva *et al.*, 2007) .

The EDAX images given the mineral composition of nano-zeolite before and after loading Zn. Mineral composition of pure zeolite consists of carbon (11.74%), oxygen (44.79%), magnesium (8.18%), aluminum (4.66%), silica (26.19%) and calcium (4.43%) (Fig. 5). The result showed that, the zinc ions was adsorbed by the zeolite and it was

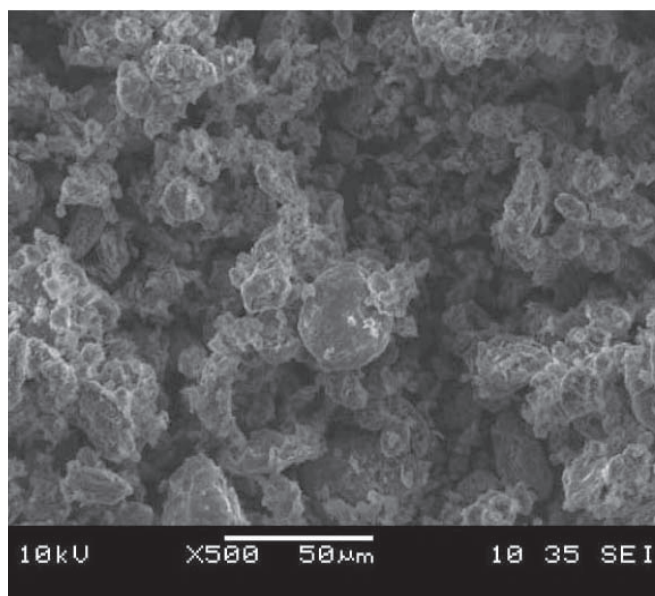


Fig. 2: Nano zeolite after loading zn

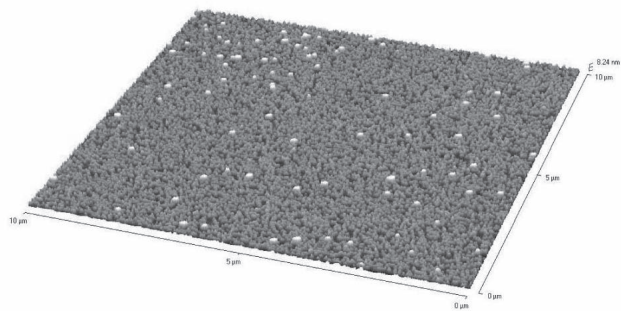
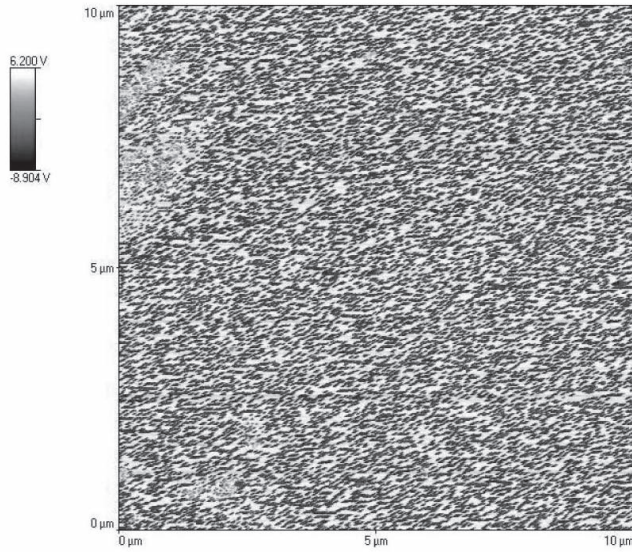
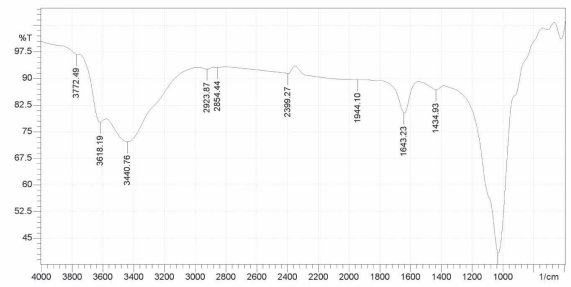
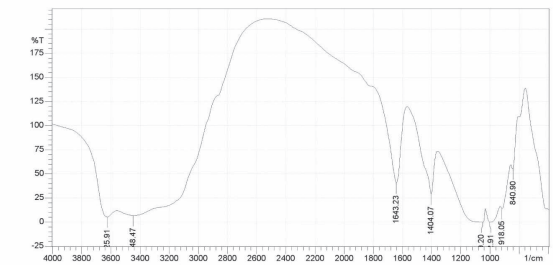


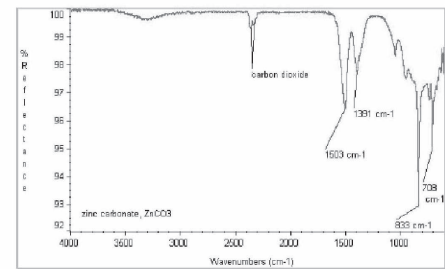
Fig. 3a: Phase image of zinc ions on zeolite  
 Fig. 3b: 3D view of zinc ions on zeolite



a. Zeolite

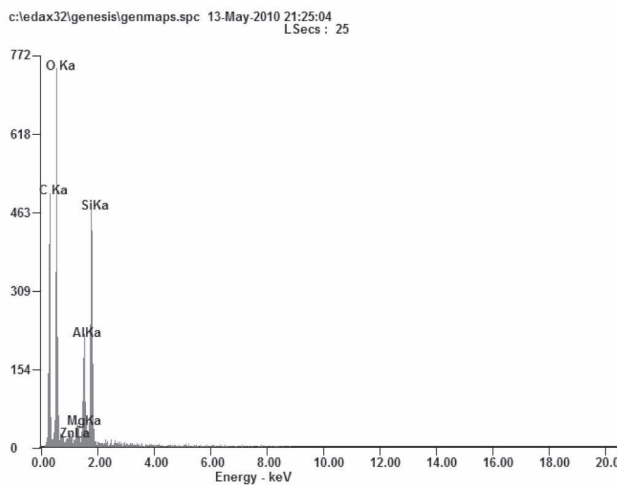


b. Zeolite+zinc



c. Reference

Fig. 4: FT-IR spectra of zeolite, zeolite loaded with zinc and the reference



Element	Wt%	At%
<b>CK</b>	45.39	57.62
<b>OK</b>	30.71	29.27
<b>ZnL</b>	00.38	00.09
<b>MgK</b>	01.20	00.75
<b>AlK</b>	06.68	03.77
<b>SiK</b>	15.64	08.49
<b>Matrix</b>	Correction	ZAF

Fig. 5: EDAX image of nano-zeolite loaded with Zn

included in the mineral composition as 0.38%. Similar results were obtained by several researchers (Ming and Allen 2006, Murat *et al.*, 2006, Patrick and Francoiz, 2008).

### Zinc Sorption

The zeolite and nano-clays montmorillonite, halloysite and bentonite were loaded with zinc sulphate of different molar concentrations (Fig. 6). The zinc sorption on nano-zeolite and nano-clays showed that the amount of zinc sorbed increases with the increase in equilibrium  $Zn^{2+}$  concentration (Murat *et al.*, 2006). This increase continues up to 4500 ppm and beyond this value, there is not a significant change at the amount of adsorbed metal ions (Patrick and Francosis, 2008). This plateau represents saturation of the active sites available on the zeolite samples for interaction with metal ions (Peric and Medvidovic, 2004). It can be concluded that the amount of metal ions adsorbed into unit mass of the zeolite at equilibrium (the adsorption capacity) rapidly increases at the low initial metal ions concentration and then it begins to a slight increase with increasing metal concentration (Sheta *et al.*, 2003). These results indicated that energetically less favorable sites become involved with increasing metal concentrations. Among them, zeolite adsorbed more zinc (220ppm) than other nano-clays, which was followed by nano-montmorillonite (175 ppm). The adsorption rate obtained with the zeolite seemed to be very satisfactory and clinoptilolite can be accepted as an efficient adsorbent for zinc removal (Subramanian and Tarafdar, 2011). The other clays nano-halloysite and nano-bentonite more or less similar amount of  $Zn^{2+}$  from the solution. Modification of clay minerals for the adsorption of  $Zn^{2+}$  has been reported by many researchers (Tiwari *et al.*, 2008, Unuabonah *et al.*, 2007, Welch, 1995).

The experimental data fitted well with the linearized form of

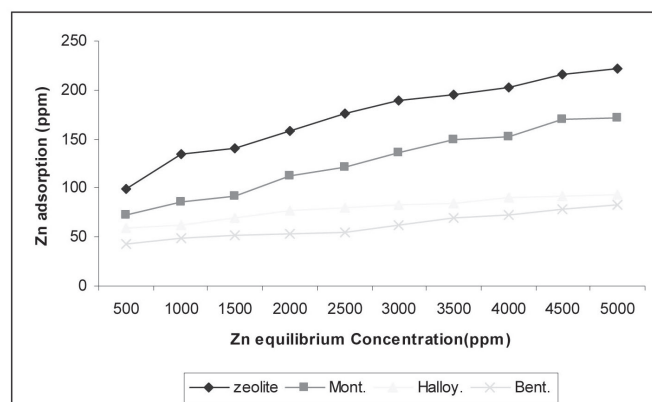


Fig. 6: Sorption zinc on zeolite and nano-clays (montmorillonite, halloysite and bentonite) under varying molar concentration of zinc sulphate

Freundlich models (Table.2). The applicability of isotherm model to the Zn-clinoptilolite system implies that both monolayer adsorption and heterogeneous surface conditions exist. The adsorption of  $Zn^{2+}$  ions on the clinoptilolite is thus complex, involving more than one mechanism. Freundlich isotherm assumes heterogeneous surface with a non-uniform distribution of heat of adsorption. The result showed that the highest sorption of  $429.5 \text{ mg kg}^{-1}$  was observed for nano-zeolite with highest bonding energy ( $0.33 \text{ mmol}^{-1} \times 10^{-3}$ ) and regression coefficient (0.99). The nano-zeolite recorded 47.9% higher adsorption than nano-montmorillonite. The nano-montmorillonite showed the adsorption of  $223.6 \text{ mg kg}^{-1}$  with the bonding energy of  $0.29 \text{ mmol}^{-1} \times 10^{-3}$ , followed by nano-halloysite  $147.3 \text{ mg kg}^{-1}$  and nano-bentonite  $93.5 \text{ mg kg}^{-1}$ . Among them, nano-zeolite adsorbed higher amount of zinc than all other nano-clays. Thus, the Langmuir isotherm provided the best correlation for modified clinoptilolite. Zeolite, which is known as the best absorbent material for heavy metals, has the highest CEC and shows high adsorption rates (Yeshchenko, *et al.*, 2005).

Table 2. Sorption Maxima (b), Bonding Energy (K), and Coefficients of Regression for Zn sorption on NC ( $r^2$ )

Nanoclays	b (mg/kg)	K ( $\text{mmol}^{-1} \times 10^{-3}$ )	$r^2$
Nano zeolite	429.5	0.33	0.99
Nano montmorillonite	223.6	0.29	0.97
Nano Halloysite	147.3	0.24	0.96
Nano Bentonite	93.5	0.20	0.94

### Slow Release of Zinc

At the start of the experiment (Fig.7), a maximum concentration of 22 ppm Zn was observed in the leachate from nano-zeolite followed by nano- montmorillonite (12 ppm), nano-halloysite (5 ppm), nano-bentonite (3 ppm) and zinc sulphate (2.5 ppm). Furthermore, it can be seen that in the initial stage,  $Zn^{2+}$  release from all the nano-clays occurred rapidly and attained a static at about 312 h, after which slow release was observed. The data revealed that the entire available Zn from zinc sulphate was exhausted after 120 h beyond which the concentration of  $Zn^{2+}$  reached below detectable limits. However, the release of zinc from nano-zeolite was continued even after 1176 h, with a concentration of 5 ppm. The same results were reported by several researchers (Zhou and Huang, 2007). It was reported that, the mechanism for this effect may be sparingly soluble minerals are dissolved by the sequestering effect of the exchanger, thereby releasing trace nutrients to zeolite exchange sites where they are more readily available for uptake by plants. Zeolites can become an excellent plant growth medium for supplying plant roots with additional vital nutrient cations and anions. The nutrients are provided in a slow-release, plant root demand-driven fashion through

the process of dissolution and ion exchange reactions. The absorption of nutrients from the soil solution by plant roots drives the dissolution and ion exchange reactions, pulling away nutrients as needed. The zeolite is then “recharged” by the addition of more dissolved nutrients. In effect, zeolites increase nutrient retention, reduce environmental nutrient losses and reduce fertilizer requirements by establishing a replenishable and balanced nutrient supply in the plant root zone.

Nano-zeolite showed leaching of zinc in three stages

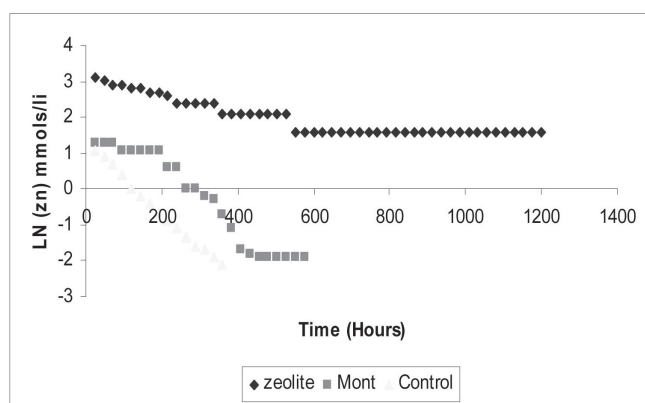


Fig. 7: Kinetics of zinc release from nano-zeolite, nano-clays and zinc sulphate

(Fig. 7). Zn levels decrease sharply in the first 220 hours ( $k_1 = 0.53$ ), and stabilize thereafter. The result also showed that from 300 to 500 hours it follows second stage ( $k_2 = 9.44 \times 10^{-3}$ ). In this stage it supplies 2 ppm of zinc. The next stage falls from 500 hours ( $k_3 = 1.7 \times 10^{-3}$ ) and it supplies 1.5 ppm of zinc and this condition is static even after 1000 hours. This may be due to the fact that, the zeolite not only increases nutrient retention but also achieves the slow release process of nutrient for gradually releasing the nutrient to the plant so as to reduce environmental nutrient losses of the soil by means of the ion exchange ability. Therefore, the natural environmental materials of the diatomite and the zeolite are mixed to be the plant growth medium for agriculture to increase crop yields.

The data suggest that the nano-zeolite based fertilizers supply Zn for an extended period of up to 40 days while such release ceased to exist within 10-12 days. The trend of Zn release pattern can be exploited in the development of nano-fertilizer that ensures sustainable plant development besides environmental safety. More research is needed to address the field response of nano-formulations and biosafety issues concerning nano-fertilizers.

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