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CHARACTERIZATION OF SLOW RELEASE OF SULPHUR NUTRIENT – A ZEOLITE BASED NANO-FERTILIZER

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ABSTRACT

An attempt was made to synthesis a Nano-zeolite based slow release sulphur nutrients and to characterize them using high resolution instruments as a confirmation note of the effort. Zeolite is a natural super porous mineral (part of group of hydrated aluminosilicates) carrying a negative charge balanced by freely moving cations with positive charges. This provides an ideal trap for positive cations which are then released that commensurate with crop nutrient requirement. Naturally occurring mesoporous material (zeolite) was reduced to a desirable nanosize (50-60nm). The nano-sized zeolite was fortified with anionic (SO₄⁻) nutrients. The zeolite loaded with or without nutrients was characterized using particle size analyzer, SEM, XRD, FTIR and Raman spectroscopy. The data have clearly demonstrated that fortification of nutrients had been successfully done as a long lasting nano-fertilizer.

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INTRODUCTION

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). They are tectosilicates exhibiting an open, three-dimensional structure containing cations needed to balance the electrostatic charge of the framework of silica and alumina tetrahedra and containing water (Hemingway and Robie, 1984). Different combinations of SiO₄ and Al (OH)₆ tetrahedral lead to the formation of a three-dimensional framework with pores and voids of molecular dimension. Shape, dimensions and linkage of zeolite pores and voids are the key characteristics of zeolite materials. The pores and interconnected voids are occupied by cations and water molecules. The structure of each zeolite mineral is complex,

but they all have large open 'channels' in the crystal structure that provide a large void space for the adsorption and exchange of cations. The internal surface area of these channels is reported to reach as much as 1300 m² g⁻¹ of zeolite, making zeolite an extremely effective ion exchange (Subramanian and Rahale, 2011). The mineral has a three-dimensional crystal lattice, with loosely bound cations, capable of hydrating and dehydrating without altering the crystal structure. Other useful chemical and physical properties include: high void volume (~ 50%), low density (2.1–2.2 g cm⁻³), excellent molecular sieve properties and high cation exchange capacity (CEC) of 150–250 c mol (p⁺) kg⁻¹ (Barros et al., 2003). Recently, Ramesh et al. (2010) suggested that there is an increasing interest in the utilization of nanoporous zeolites in farming over the years because of current public concern about the adverse effects of chemical fertilizers on the agro-ecosystem. Ion-exchange properties of zeolites are recognized as important for plant nutrition due to their high cation-exchange capacity and porosity. Both ion-exchange and porosity are relevant to agronomy and soil science. The specific structure and diversity of the zeolites vary as also their application. They can be used either as

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carriers of nutrients and/or a medium to free the nutrients. There are reports of urea impregnated zeolite chips, which can be used as slow release nitrogen fertilizers. Li (2003) demonstrated the feasibility of using Surface-Modified Zeolite (SMZ) using hexa decyltrimethylammonium (HDTMA) as a nutrient carrier to control nitrate release, and concluded that SMZ is a good sorbent for nitrate, whereas slow release of nitrate is achievable. The high potential of zeolitic minerals as nitrogen fertilizers has been demonstrated. Their use would diminish environmental problems and increase fertilizer efficiency. Studies using natural zeolites have demonstrated significant improvements in fertilizer efficiency for zeolites compared to soluble salts (clinoptilolite is 7–9 times more efficient than KNO_3) (Ming and Allen, 2001). This present day study is about the synthesis and characterization of surface modified nanozeolite and its properties has a slow release fertilizer having a promising effect in agriculture.

MATERIALS AND METHODS

The studies were conducted at Department of Nano science and technology, Tamil Nadu Agricultural University, Coimbatore, India.

Synthesis of nano- fertilizer

The natural zeolite (clinoptilolite) was purchased from GM Chemicals, Ahmedabad, Gujarat. Initially, the zeolites were in the dimension of 1-2 μm . The ball milling was used to bring the material to the nano size. The zeolite material was taken in 1:20 (sample and ball ratio) in vials and 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.

Surfactant modification of zeolite

Negative charges of the zeolite nanoclay were modified by treating them with a surfactant hexadecyltrimethylammonium bromide (HDTMABr) (M/s.Sigma Aldrich, Bangalore) as suggested by Bansiwala *et al.* (2006). A preweighed quantity of zeolite 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 pestle and mortar to a fine particle size.

Fortification of nutrients

The sources of nutrient are gypsum for sulphur. 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°C. The sample was shade dried and powdered and it has been used as a fertilizer source.

Characterization of nano-zeolite

The zeolite loaded with and without nutrient were characterized using particle size analyzer, SEM, XRD, FTIR and Raman spectroscopy.

RESULTS AND DISCUSSION

Characterization of Size of Zeolite

The data have shown in the Fig.1 that the size of the nano-zeolite varied from 50 – 70 nm with an average dimension of 60 nm. Originally the size of the zeolite was 1000 – 7000 nm which had been reduced to the desirable dimension of 60 nm after ball milling. The result is in agreement with the observations of Bansiwala *et al.* (2006). The nano-zeolite exhibited higher surface area (1300 $\text{m}^2 \text{g}^{-1}$) and area get gradually decreased after fortification of nutrients is nano-composite (900 $\text{m}^2 \text{g}^{-1}$). The data are in support of Holister *et al.* (2003) who have reported that the increase in the surface area to the volume ratio, which is a gradual progression as the particle got reduced to lead to an increasing dominance of the behaviour of atoms on the surface of a particle over that of those in the interior of the particle

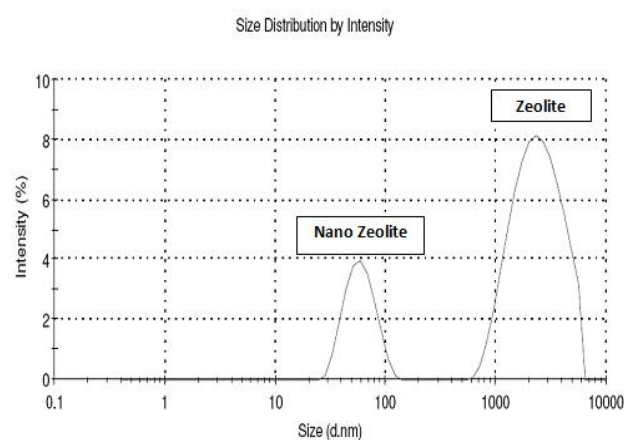


Fig. 1. Particle size distribution of zeolite and nano-zeolite

Characterization of nano-zeolite before and after loading of SO_4^{3-} ions

Characterization using SEM

The surface morphology of surface modified nano zeolite was examined under SEM. The result showed that the surface morphology of surface modified nano zeolite before and after loading with SO_4^{3-} . The Plate 1a shows that the nano-zeolite was cubical to round shape. The Plate.2b showed that the SO_4^{3-} ions was attached to the nano-zeolite which was rod shaped. Moreover, after the attachment of SO_4^{3-} ions there was a reduction in the surface area of nano-zeolite. The surface area was reduced from 1300 to 1000 mg g^{-1} . The same result was reported by Kosanovic (1997). The SEM images of montmorillonite were also given by Tabernero *et al.* (2010).

Characterization using X-Ray Diffraction

The XRD pattern of zeolite before and after loading SO_4^{3-} is given in Fig 2a and 2b. The peaks at $2\theta = 20.66, 30.83, 35.23, 41.27, 50.46, 59.52$ and 73.37 was observed for pure zeolite (Fig 1a.). When it was loaded SO_4^{3-} , there was change in peaks ($2\theta = 10.72, 21.05, 29.71, 43.57, 49.76, 56.73, 76.59, 85.19$) (Fig 1b). There was a change in the peak angle and these peaks clearly showed that SO_4^{3-} was attached on zeolite. Marcus *et al.* (2006) revealed a similar characterization pattern of X-Ray Diffraction for Mechanically Alloyed Tripotassium Sodium Sulfate.

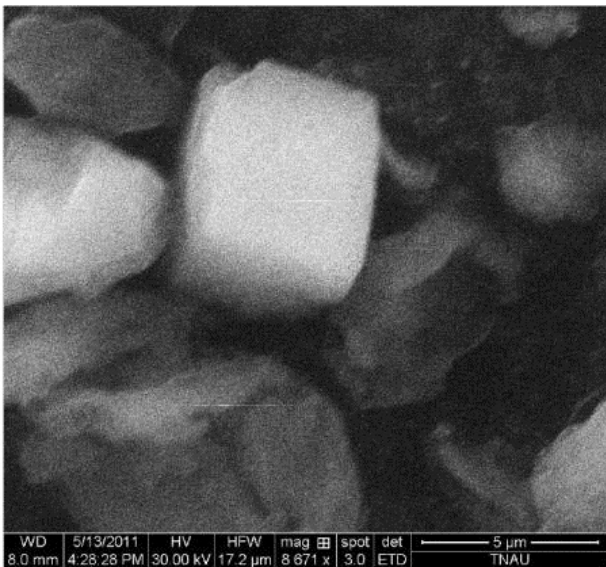


Plate 1a. SEM image of the nano-zeolite before loading of nutrients

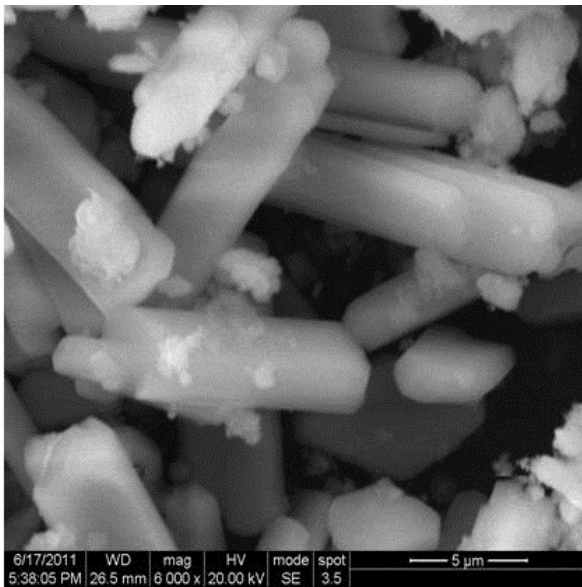


Plate 1b. SEM image of the nano-zeolite after loading of SO_4^{3-}

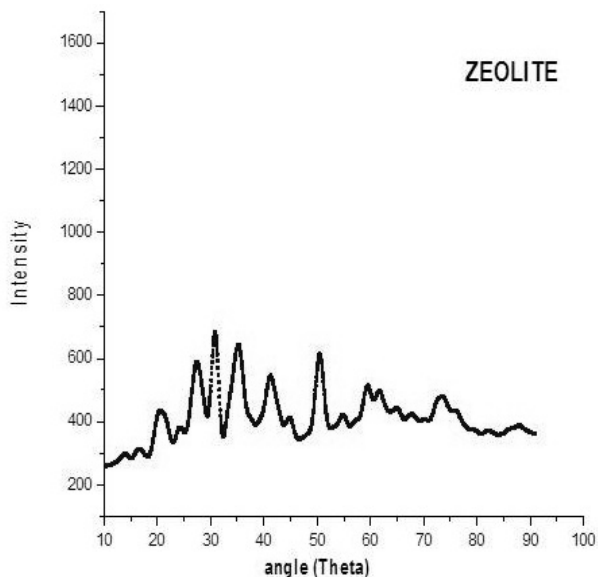


Fig. 2a. XRD pattern of nano-zeolite

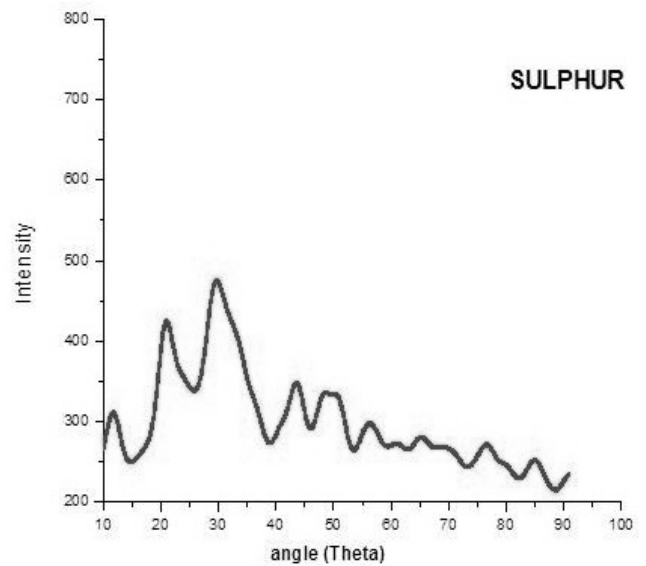


Fig. 2b. XRD pattern of nano-zeolite loaded with SO_4^{3-} ions

Characterization using Raman spectrum

The Raman spectrum was studied for the nano-zeolite unloaded and sulphur loaded is given in the Fig 3. The relative intensities of the peaks were used to quantify the information on the composition of a mixture. The Fig 3a showed that the intensity of peaks for pure zeolite were 371.2, 520.9, 568, 1641.4, 1694.1, 1742.8, 1779.3, 1887.1, 1965.7 and 2048 cm^{-1} .

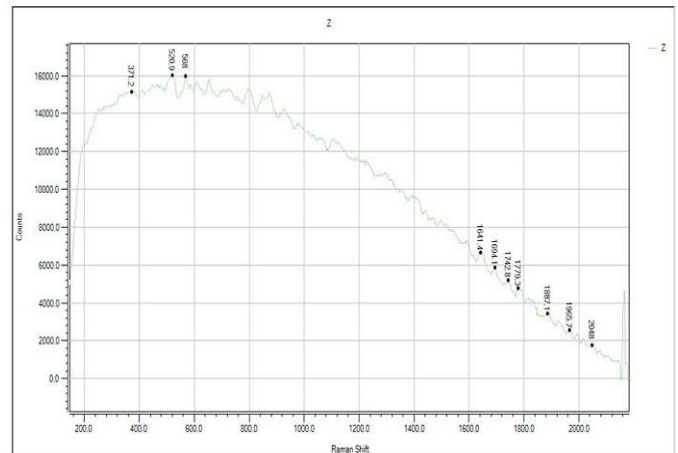


Fig. 3a. Raman spectra of nano-zeolite before loading nutrients

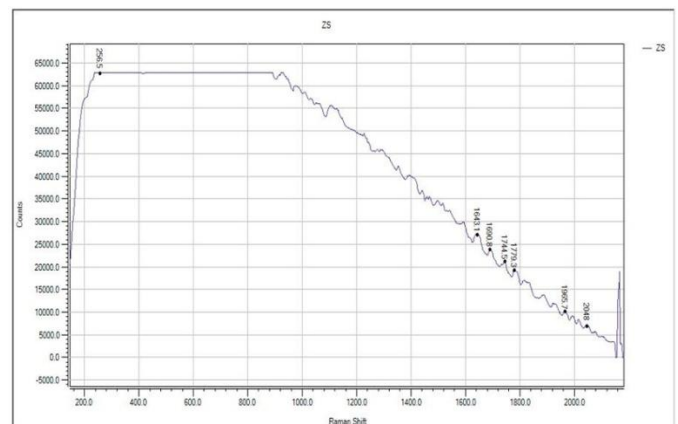


Fig. 3b. Raman spectra of nano-zeolite after loading SO_4^{3-} ions

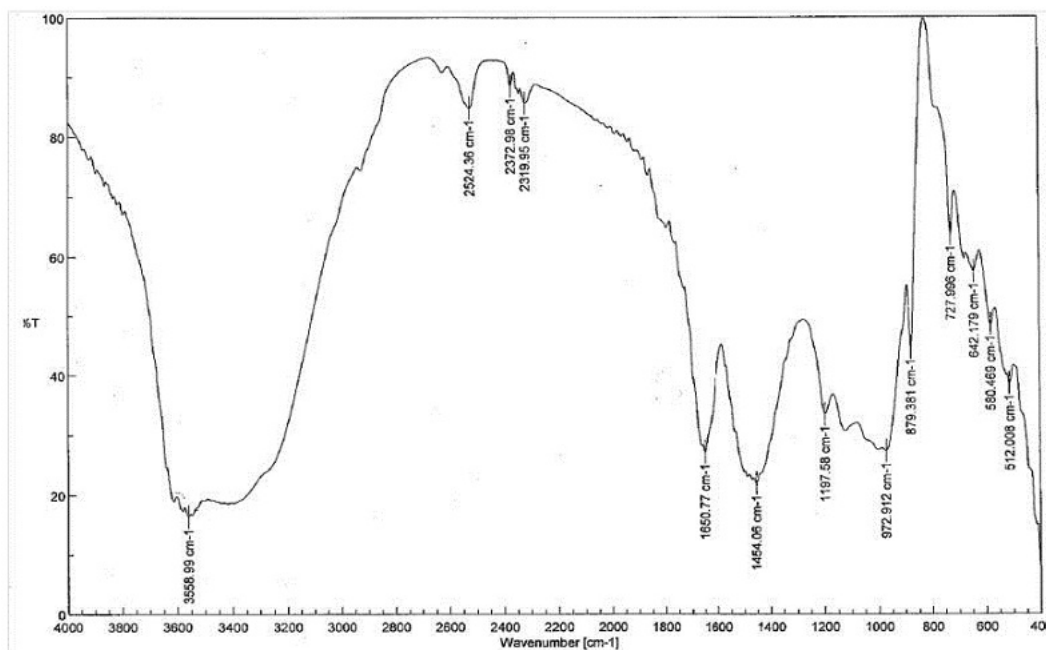


Fig. 4a. FT-IR spectra of nano-zeolite before loading nutrients

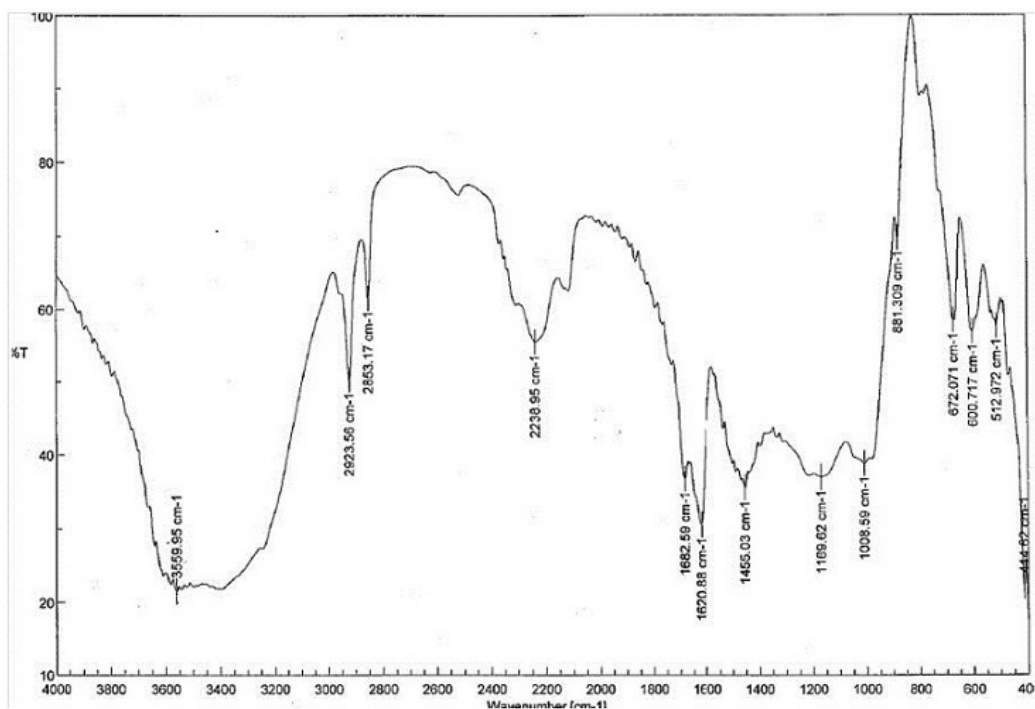


Fig. 4b. FT-IR spectra of nano-zeolite after loading with SO_4^{3-} ions

The same way the peaks for zeolite loaded sulphur were 256.5, 1643.1, 1690.8, 1744.5, 1779.3, 1965.7 and 2048 cm^{-1} (Fig 3b) which confirmed sulphur attachment with zeolite. Similarly, Pradip *et al.* (2008) revealed that the Raman spectroscopy of the controlled release of nano-fertilizer, prepared at different sulphate concentrations by using a green laser with an excitation wavelength of 532 nm and power of 14.4 mW in a range of Raman shift from 1100 to 1800 cm^{-1} .

Characterization using FT-IR Spectra

The data were confirmed with FT-IR spectra which were given in the Fig 4. The IR spectra of nano-zeolite unloaded were given in the Fig 4a. which has characteristic peaks of (1454.06, 2372.98, 3558.99 cm^{-1}). The IR spectra of nano-

zeolite loaded SO_4^{3-} ions were given in the Fig 4b. which has characteristic peaks of (1169.62, 1682.59, 2853.17, 2920 cm^{-1}). Since there was shift in the peaks after loading of SO_4^{3-} ions. This confirms that the SO_4^{3-} ions were attached into nano-zeolite. The changes in FT-IR peaks due to modification of zeolite were obtained by several researchers (Nichol *et al.*, 1990; Picos *et al.*, 2010; Kamaruddin, 2008).

Conclusion

This studies clearly demonstrated that among the nano-particles, nano-zeolite response to slow release of fertilizer because of its higher surface area retain and release anionic (SO_4^{3-}) in a slow and steady state. The characterization using high resolution microscopes such as SEM, XRD, Raman

spectrum and FT-IR confirmed that they can act as the carrier for the nutrient.

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