Synthesis and Characterization of Surface Modified Nano-Zeolite Fortified with Sulphate and its Sorption and Desorption Pattern

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Received 26 July 2014; revised 14 June 2015; accepted 10 October 2015

A laboratory study was undertaken in a ball milled natural zeolite (92.6 nm) in order to develop a surface modified nano-zeolite (SMNZ) for slow release of sulphate that can be used in crop production system. The nano-zeolite was surface modified with 135 mM concentration of hexadecyltrimethylammoniumbromide (HDTMABr) for adsorption of anion on zeolite’s surface. On surface modification, imaging the surface morphology of nano-zeolite by Scanning Electron Microscope (SEM) it was irregular flake like structure. The quantity of SO$_4^{2-}$ adsorbed ranged from 24.45 to 495.66 mM and 7.5 to 639.37 mM and desorbed in the range of 0.38 to 27.01 mM and 0.39 to 48.17 mM SO$_4^{2-}$ for zeolite and SMNZ, respectively. Our data clearly demonstrated that the surface modified nano-zeolite facilitates both higher retention (29%) and release (77%) of SO$_4^{2-}$ in comparison to conventional zeolite.

Keywords: Synthesis, Nano-Zeolite, Surface Modification, Characterization, Sulphate, Sorption, Desorption

Introduction

The deficiency of available status of sulphur in India has increased to 46% of the arable lands causing considerable reduction in yield and quality of crops particularly oilseeds. Nanotechnology is a power tool to manipulate at the atomic or molecular scale to regulate the release of nutrient ions from the fertilizer carrier so as to supply nutrients that commensurate crop demand. Nano-fertilizer are synthesized by fortifying nutrient ions in the adsorbents that can regulate the release to the rhizosphere target. The present study deals with the synthesis of nano-zeolite by top down approach using high energy ball mill and surface modified using HDTMABr. The characterizations of zeolite, unmodified nano-zeolite, surface modified nano-zeolite and sulphate loaded SMNZ were carried out using Particle Size Analyzer, Zeta Analyzer, Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR), and Energy Dispersive X-ray Spectroscopy (EDS) and finally to study the sorption and desorption of zeolite and surface modified nano-zeolite with various concentration of sulphate.

Materials and methods

Materials

The natural zeolite used in this study was epistilbite [Ca$_3$ (Al$_6$Si$_{18}$O$_{48}$).16H$_2$O], purchased from GM chemicals, India. In order to load the SO$_4^{2-}$ ions, the negative surface charge of zeolite was modified by hexadecyltrimethylammoniumbromide (HDTMABr) (Sigma Aldrich Chemicals). Ultrapure distilled water was used throughout the experiments. The initial zeolite properties such as pH, EC, bulk density, particle density, porosity, cation exchange capacity (CEC), zeolite colour and SiO$_2$/Al$_2$O$_3$ molar ratio were determined using standard protocols. The data and standard protocols are furnished in Table 1.

<table>
<thead>
<tr>
<th>Properties of Zeolite</th>
<th>Measured values</th>
<th>Standard methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite pH</td>
<td>8.9</td>
<td>Potentiometry method$^{1,1}$</td>
</tr>
<tr>
<td>Zeolite EC</td>
<td>0.94 dSm$^{-1}$</td>
<td>Conductimetry method$^{1,1}$</td>
</tr>
<tr>
<td>Bulk density</td>
<td>0.57 g cc$^{-1}$</td>
<td>Cylindrical method$^{1,2}$</td>
</tr>
<tr>
<td>Particle density</td>
<td>0.66 g cc$^{-1}$</td>
<td>Cylindrical method$^{1,2}$</td>
</tr>
<tr>
<td>Porosity</td>
<td>65.1 %</td>
<td>Copper (II) ion with Triethylenetetramine and Tetaethylpentamine$^{1,3}$</td>
</tr>
<tr>
<td>CEC</td>
<td>190 meq 100 g$^{-1}$</td>
<td>Munsell colour chart$^{1,4}$</td>
</tr>
<tr>
<td>Zeolite colour</td>
<td>Dry - 5YR 7/1</td>
<td>Ammonium chloride$^{1,5}$</td>
</tr>
<tr>
<td>SiO$_2$/Al$_2$O$_3$ molar ratio</td>
<td>Moist - 7.5YR 7/2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wet - 10 YR 7/3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.94</td>
<td></td>
</tr>
</tbody>
</table>

— Table 1 —

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Synthesis of Nano-Zeolite (NZ)

Natural epistilbite zeolite was sieved through an analytical sieve of 0.5 mm mesh size. Nano-epistilbite was synthesized using a high energy ball milling (Fritsch-pulverisette 7, Germany). The milling was done in dry condition. During the course of experimentation, the milling conditions such as speed, duration and ball to powder ratio were standardized to reach size reduction and crystallinity retention. Accordingly, the milling speed, duration and balls to powder ratio were set as 600 rpm, 6 hours and 1:10, respectively. After six hours of ball milling of natural zeolite, the particle size was reduced and also the crystallinity was maintained. The procedure of ball milling followed in our work is similar to the procedure followed by Alizera et al. who have reported that the nano-zeolite can be achieved by dry milling using a planetary ball mill.

Surface Modification of Nano-Zeolite (SMNZ)

The surface modification of nano-zeolite was done using a surfactant hexadecyltrimethylammonium-bromide. Each 250 ml shaking bottle was added with 60 g of nano-zeolite and 180 ml of 135 mM HDTMABr solution and mixed on a reciprocal shaker for 24 hours at 150 rpm. Thereafter, the mixture was centrifuged at 5000 rpm for 20 minutes. The solid portion of nano-zeolite after treated with various concentration of HDTMABr solution was dried for two weeks and the surface modification of nano-zeolite was confirmed.

Sorption and desorption of zeolite and SMNZ

Zeolite and surface modified nano-zeolite were treated with various concentration of ammonium sulphate viz., 0, 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 mM. In this study, three grams of zeolite or surface modified nano-zeolite was taken and added 30 ml of sulphate solution and then it was shaken in an orbital shaker for 12 hours at 150 rpm. The samples suspension was centrifuged at 9000 rpm for 20 min. The supernatant solution was collected and used for sorption studies and the solid samples were dried for seven days and used for desorption studies. Concentration of sulphate in solid and supernatant samples was analyzed by barium chloride methods.

Characterization of zeolite and surface modified zeolite

Particle size analyzer

The particle size distribution of the zeolite was obtained by laser diffraction method using particle size analyzer (Horiba, SZ-100). In the particle size analyzer, particle size measured by photon correlation method in the range of 0.30 nm to 8.00 µm and a data acquisition time is less than two minutes. The cell holder temperature can be controlled from 1 to 90 °C whereas for electrode and plastic cell it was 1 to 70 °C. The particle size measurement was done at 90 or 173 degree angle. During experiment, 10 mg of sample was taken in a beaker and 50 ml of ultra pure water was added and sonicated for 30 min. in ultra sonicator. Then size distribution of samples was measured using particle size analyzer.

Zeta Analyzer

Zeta potential measurement for the zeolite, unmodified nano-zeolite and surface modified nano-zeolite were determined using a zeta analyzer (Horiba, SZ-100). In the zeta analyzer, zeta potential measurement varied from -200 mV to 200 mV. In the zeta analyzer, laser light is divided into two beams as input light and reference light. Scattered light by sample particles and reference light modulated by the modulator interfere in the prism are detected. The detected signals are changed into digital signal to be calculated. The sample preparation for zeta potential measurement was same of the particle size analyzer.

Scanning Electron Microscope

The surface morphology of zeolite was studied in a scanning electron microscope (SEM-FEI-Quanta 250). The few milligram of sample was initially placed on carbon tape of stub and it was kept in a vacuum chamber for coating with a thin layer (few nanometres) of gold (Au) using sputter coater. Elemental composition and mineralogical structure of the zeolite was determined by Energy Dispersive X-ray Spectroscopy (EDXS) using diffraction equipment indicating the main mineral phases of its crystalline structure.

Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra of zeolites were recorded using a SHIMADZU (Kyoto Japan) equipped with a MCT detector. Two fifty six scans were recorded with a resolution of 4 cm⁻¹. The most useful infrared region
for zeolite characterization was lied between 4000 and 500 cm\(^{-1}\).

**Statistical analysis**

All measurements were made in triplicate and all values were expressed as the mean ± standard error of the mean. The results were subjected to an analysis by Student's t-test for mean comparison. The results were considered statistically significant if the \(p\) value was ≤0.05.

**Results and Discussion**

**Particle size analysis of Zeolites**

The particle size of zeolite, nano-zeolite and surface modified nano-zeolite were 3311.2 nm, 92.6 nm and 110.4 nm, respectively. The size distribution analyses showed that 85% of the particles have measured nano-dimension of 92.6 nm. The data clearly indicated that the top down approach (ball milling) helped to reduce the dimension of the zeolite by 33 times as that of initial dimensions. The results corroborate with the findings in the literature suggesting that the ball milling is one of the easiest mechanical methods to achieve nano-dimension\(^8,12\). Further, our data have shown that the particles are homogenous to the tune of 85% suggesting that the substrate can be used for fortification of nutrients.

**Surface charge of the particles by Zeta Analyzer**

Zeta potentials of the unmodified nano-zeolite (Figure 1a) and surface modified nano-zeolite (Figure 1b) were (-) 65.9 mV and (+) 59.9 mV, respectively. The data clearly indicated that the surface modification using HDTMBr surfactant has changed the –ve charge to +ve charge that may facilitate retention of anionic nutrients such as SO\(_4\)^{2-}. These observations are in conformity with the findings of Bowman\(^13\) who have stated that the surfactant molecules form bilayers on zeolite external surfaces with the lower layer held by electrostatic interaction between the negatively charged zeolite surface and the positively charged surfactant head groups. On the other hand, the upper layer is bound to the lower layer by hydrophobic forces between the surfactant tail groups in both layers. 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.

**Morphological analysis of Zeolites by SEM**

SEM images indicated that the morphology of zeolite can be recognized as a form of larger agglomerates with irregular flakes shape. Nano-zeolites were spherical shape while SMNZ were irregular flakes and the data closely coincide with the observations of Ramesh et al\(^8\) who have reported that nano-zeolite are spherical in shape and on surface modification it was turn as irregular like shape. Our data suggest that the ball milling is appropriate to produce nano-zeolite with desirable crystalline structure.

![Fig 1](attachment:image.png)
EDS-analysis of Zeolites

The elemental composition of zeolite, nano-zeolite, surface modified nano-zeolite and sulphate loaded SMNZ were obtained by Energy Dispersive X-ray Spectroscopy (EDS). The results on EDS showed that surface modified nano-zeolite retained 14.5% S which also confirmed with a conventional analytical method of estimating total S content of synthesized nano-based S carrier. Further, one of the cationic nutrients Ca has drastically reduced from 51.7% in the surface modified zeolite to just 3.17% after the fortification of S. This suggests that negatively charged SO₄²⁻ ions may have occupied the major portion of the surface leaving less space for Ca to get adsorbed.

FT-IR studies of zeolites

The FT-IR data indicated that the spectrum of the zeolite and unmodified nano-zeolite had characteristics peaks at wave numbers of 3554.81, 2337.45, 1813.91, 958.62 and 645.45 cm⁻¹, and 3552.53, 1476.70, 1079.25, 975.27, 486.50 and 444.63 cm⁻¹, respectively, whereas the surface modified nano-zeolite had characteristics peaks at wave numbers of 3353.99, 2925.78, 2855.50, 2524.46, 1656.74 and 727.99 cm⁻¹ which indicates the incorporation of HDTMABr onto the zeolite surface. Although there are some slight shifts in the peaks position at each wave numbers in spectra of zeolite and unmodified nano-zeolite, both of the patterns are nearly the same, showing unchanging of the zeolite structure during the HDTMABr loading. Particularly, the presence of peaks at 2924.09 and 2854.65 cm⁻¹ in the surface modified nano-zeolite spectrum (related to C-H and C-C vibrations in the surfactants, respectively), that are absent in the zeolite and unmodified nano-zeolite spectrum, confirms the loading of HDTMABr onto the surface modified nano-zeolite. Stronger hydrogen-bonded interactions (e.g. in hydroxyl nests) results in a very broad absorption band in the 3650-3200 cm⁻¹ range. In the zeolite, this large absorption band was assigned to bridged hydroxyl groups which are perturbed by hydrogen bond interactions with the zeolite framework. Bridging hydroxyl groups, which are the active sites in catalysis, are found in wave number ranges from 3580-3530 cm⁻¹. The high frequency range corresponds to OH groups vibrating in large cavities, formed by pores larger than eight-membered rings, whereas in smaller voids the low-frequency range is observed. This is typical for zeolite, which shows OH bands around 3550 cm⁻¹, the actual frequency depending on the Si/Al ratio.

Sorption study of Zeolite and Surface Modified Nano-Zeolite

Results of sulphate adsorption of zeolite and surface modified nano zeolite studies are given in Table 2. There was an almost linear increase in sulphate adsorbed with every increase concentration of added ammonium sulphate solution from 100-1000 mM in zeolite and surface modified nano zeolite. The amount of sulphate adsorbed by zeolite and surface modified nano-zeolite ranged from 24.45 to 495.66 mM and 7.5 to 639.37 mM sulphate, respectively. The nano-zeolite adsorbed 23% more sulphate ions which may be due to the preferential adsorption at the positive sites of the clays and on surface modification of clay provided positive charge for anionic nutrient adsorption and further confirmed by Sudhakar and Sridharan who have reported that the sulphate ion apparently adsorbed by ligand exchange as well as by retention as a counter ion in the diffuse double layer. The sulphate ion adsorbed on zeolite as a binuclear bridging complex.

Desorption of Zeolite and Surface Modified Nano-Zeolite

Various concentration of ammonium sulphate 0 to 1000 mM was used in zeolite and nano-zeolite for sulphate desorption experiment (Table 2). Among the various concentrations, the quantity of desorbed sulphate ranged from 0.38 to 27.01 mM and 0.39 to 48.17 mM sulphate for zeolite and nano-zeolite, respectively. Desorption of sulphate from zeolite and nano-zeolite has increased linearly to the tune of 77% when the equilibrium sulphate concentration.
was maintained at 1000 mM. This may be due to the extensive surface area of nano zeolite to retain nutrients. The nano-clays particularly montmorillonite and nano-zeolite had the extensive surface area of 1000 and 1300 m² g⁻¹, respectively and they had retained abundance of nitrate nitrogen and the desorption was slowly, steadily for a longer period of time²¹.

Conclusion
Our study has clearly indicated that the surface modified nano-zeolite is capable of retaining SO₄²⁻ up to 640 mM concentration. Such nano-zeolite based fertilizer had 14.5% S that has been confirmed by EDS and conventional analytical methods. The characterization of nano-formulation done in SEM and FT-IR has confirmed the loading pattern of nutrients. Sorption and desorption studies have demonstrated that the surface modification of nano-zeolite has a potential to alter the retention and release of SO₄²⁻ that may serve as a base data to design and fabricate slow release S fertilizer.

Acknowledgements
The authors are grateful to Department of Science and Technology (DST), Government of India, New Delhi, for sponsoring a DST Nano Mission Project “Fabrication of Nano-Agricultural Inputs for Groundnut Productivity and Environmental Safety” (NS 89 / 2010).

References