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SORPTION CHARACTERISTICS OF NANO ZEOLITE BASED SLOW RELEASE SULPHUR FERTILIZER

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ABSTRACT

Understanding the sorption process in natural zeolites is necessary for effective utilization of these minerals as nutrient adsorbents and consequently as controlled releases of plant nutrients. This research was undertaken to characterize the ability of natural zeolites minerals to adsorb and release sulphur. The potential for sorption of these ions were evaluated by applying the Langmuir equations. Thus a percolation reactor experimental setup was used to study the sorption, desorption pattern of nutrients. The nano-zeolite has been fortified with a sulphur source (Gypsum). Nano-fertilizer formulation is capable of releasing nutrients to the tune of 1000-1200 hrs while conventional fertilizer could release only up to 300-350 hrs. The data suggested that nano-formulation will be very ideal to regulate release of nutrients. This project is one of the pioneering attempts to synthesis zeolite based fertilizer formulation to regulate the nutrient release.

INTRODUCTION

In recent times, concerns about unbalanced use of fertilizers leading to environmental pollution have been globally expressed. As a result, studies on how to use efficient methods to reduce nutrient applications at the same time increasing or maintaining crop yield, reducing nutrient losses and improving nutrient use efficiency are imperative (Oosterhuis and Howard, 2008). For instance, sustainable nutrient use efficiency could be attained by agronomic practices which take into account timely synchronization of nutrient application with plant roots development, or use of slow-release fertilizers, and foliar feeding (Matson *et al.,* 1997; Oosterhuis and Howard, 2008). Nanotechnology applications in agriculture are gradually transforming the theoretical possibilities into the practical applications. Zeolite is a natural super porous mineral (part of group of hydrated alumino silicates) carrying a negative charge balanced by freely moving cations with positive charges; this provides an ideal trap for positive cations such as ammonium and potassium which are then released that commensurate with crop nutrient requirement. They are among the most common minerals in sedimentary rocks and are reported to be especially common in tuffaceous rocks (Sheppard and Mumpton, 1981). Oliveira and Rubio (2007) reported the sulphate ions adsorption showed a high process kinetic followed by a first-order reaction kinetic model and the data fitted a Langmuir isotherm model. Removal of sulphate from aqueous solution by modified clinoptilolite showed a strong adsorption on HDTMA (hexadecyl–trimethyl–ammonium)–zeolite (Haggerty and Bowman, 1994). The nano-zeolite presents a leaching pattern, which is in accordance with that of an SRF, characterized by two stages in which a first-order kinetic law describes the release process (Bansiwal et al., 2006 and Kinjo *et al.*, 1971). Several applications have been identified in zeolite research and attempts are being made worldwide. Considerable research has been carried out globally to exploit the potential of zeolites in the perpetual maintenance of soil productivity. The current growing awareness of the phenomenon and availability of inexpensive natural zeolites has aroused considerable commercial interest and also, a number of issues have been identified for research to develop zeolite based nano- fertilizer. Sulphur is now

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recognized as major plant nutrients, along with macronutrients. It is essential for the growth and development of all crops and this essential sulphur has been absorbed in the form of sulphate (SO_4^{-2}) through roots by most of the plants. Nowadays, sulphur deficiency has been reported widely and in most of the cases it plays an important role in restricting yield, produce quality, nutrient efficiency and so on. So this work has been concentrated on increasing the use efficiency of sulphur and to synthesis nano- zeolite based slow release sulphur fertilizer.

MATERIALS AND METHODS

The studies were conducted at Department of Nano science and technology, Tamil Nadu agricultural university, Coimbatore.

Synthesis of nano- fertilizer

The natural zeolite (clinoptilolite) was purchased from GM Chemicals, Ahmedabad, Gujarat. Initially, the zeolites were in the dimension of 1-2µm. 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 Bansiwal *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 37^0C. The sample was shade dried and powdered and it has been used as a fertilizer source.

Sorption and Desorption of nutrients from nano-zeolite

A percolation reactor experimental setup was used to study the sorption, desorption pattern of various nutrients from nano-composites using apparatus designed after **Hemandez *et al*., 1994.**

Sorption experiment

To study the sorption behavior of sulphur on surface modified zeolite, to each 50-ml centrifuge tube, 1 g of surface modified zeolite and 50 ml of 0.5, 1.0, 1.5, 2.0, 2.5 M calcium sulphate solution were mixed for 24 h at 150 rpm (Li, 2003). The mixtures were then centrifuged and the solution was filtered and sulphate concentration was determined by turbidimetric method. The amount of sulphate content was calculated from the difference between the initial and equilibrium solution concentrations.

Determination of sulphate

About 5ml of filtrate was taken in a 25ml volumetric flask and exactly 10 ml of sodium acetate acetic acid buffer, 1 ml of gum acacia and 1 g of barium chloride added. Make up the volume with distilled water and shake well. The absorbance was read in spectrophotometer at 400 nm after adjusting the meter to zero with the blank. The sulphate content was calculated by referring the standard curve.

The sorption of anionic species by the Langmuir equation

The sorption of anionic species on zeolitic surfaces can be well-described by the Langmuir equation (1916) as follows.
$C/x/m = 1/k + c/b$

Where,

C = Equilibrium P concentration (µg ml^{-1})
x/m = P adsorbed (mg kg^{-1})
b = Adsorption maxima (mg kg^{-1})

Desorption experiments

Preparation of Slow Release Fertilizers (SRFs)

To each 50ml centrifuge tube, 1 g of surface modified Nano-zeolite were stirred with 50 ml of 1.5 M calcium 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 sulphate loaded zeolite nano-clays. Similarly, nutrient loading was also carried out on unmodified zeolite to study the effect of surface modification on nutrient adsorption and slow release of nutrients as compared to surface modified zeolite nano-clays.

Experimental design for nutrient release

The chemical reactor designed for a constant flow of solution in several studies concerning zeolites Hemandez *et al.* (1994) was used. By this technique, heavy pluviometer regimes is simulated, which provides adequate conditions to evaluate the nutrient-supply capacity of slow release fertilizers. The chemical reactor consists of a Teflon cylinder (internal diameter= 2.5 cm, height = 15 cm) through the top of which deionized water is continuously pumped at a flow rate of 66 ml per day. Inside the reactor, 5 g of soil overlaid with the fertilizer were placed. Solutions were collected to determine sulphur content. The mean temperature during the experiment was 25 ± 0.2°C. With the nutrient loaded nano-zeolite, the characterization, nutrient release patterns were studied.

RESULTS AND DISCUSSION

Kinetics of sulphur – Sorption and desorption

Sulphate sorption

The nano-zeolite was loaded with calcium sulphate of different molar concentrations. The sulphate sorption on surface modified nano-zeolite showed that, the amount of sulphate sorbed increases with the increase in equilibrium sulphate concentration.

Sulphate sorption by Langmuir equation

The sorption of sulphate on nano-zeolite surfaces can be well-described by the Langmuir equation and the result is given in the (Table 1 and Fig. 1). The result showed that the highest sorption of 28.571 mg kg^{-1} was observed for nano-zeolite with highest bonding energy (k=1.590) and regression coefficient (r^2=0.999). The Langmuir model assumes that the adsorption occurs in surface sites where the energy is equal in each site. Langmuir equation correspond to the monolayer capacity attained at high concentrations and the equilibrium constant, respectively (Cooney, 1999).

Table 1. Sorption Maxima (b), Bonding Energy (K), and Coefficients of Regression for nutrient sorption on SMNC (r^2)

Nanoclay	b (mg/kg)	K (mmol^{-1}x 10^{-3})	r^2
Unmodified zeolite	143.6	0.23	0.94
Nano-zeolite loaded SO$_4^{3-}$	28.571	1.59	0.99

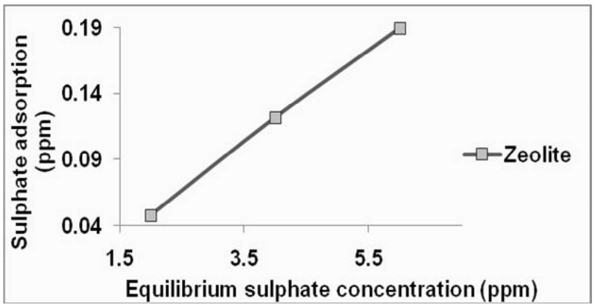

Fig. 1. Sorption Sulphate on zeolite under varying molar concentration of calcium sulphate

Slow release of sulphur

The sulphate release from nano-zeolite and pure calcium sulphate is given in the Fig. 2. It can be observed from the data that at the start of the experiment, the maximum concentration of 23.52 ppm was observed in the leachate from nano-zeolite followed by pure calcium sulphate (20.83 ppm).

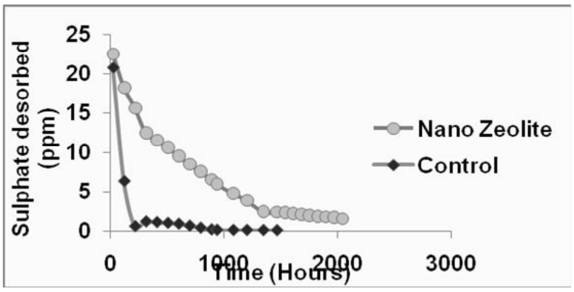

Fig. 2. Sulphate release from nano-zeolite and calcium sulphate

Furthermore, it can be seen that in the initial stage, sulphate release occurs rapidly and attained a concentration at about 350 h, after which slow release is observed. The data revealed that the SO$_4^{-3}$ in calcium sulphate was exhausted after 300 h beyond which the concentration of sulphate reached below undetectable limits. However, the release of sulphate from nano-zeolite was continued even after 2100 h, with concentrations ranging from 1.5- 1.65 ppm. Oliveira and Rubio (2007) reported the sulphate ions adsorption showed a high process kinetic followed by a first-order reaction kinetic model and the data fitted a Langmuir isotherm mode. Removal of sulphate from aqueous solution by modified clinoptilolite showed a strong adsorption on HDTMA (hexadecyl–trimethyl–ammonium)–zeolite (Haggerty and Bowman, 1994).

Kinetics of sulphate release

From the release of sulphate, kinetics of sulphate release was calculated. Fig. 3 showed the kinetics of sulphate release from nano-zeolite and calcium sulphate. The results showed that the release takes place in different stages. However, the release of calcium sulphate was characterized by a steep slope with a decay time of 600 h after which the sulphate concentration reaches below detectable limits whereas the nano-zeolite also showed leaching of sulphate in two stages. At the initial stage the sulphate release was faster till 600 h and then the sulphate release curve was stabilized progressively. However, from 600 h onward a sulphate concentration of about 0.3 ppm is continued even after 1520 h. Oliveira and Rubio (2007) reported that the kinetic of sulphate ions adsorption was determined following the same experimental procedure described above and varying the contact time.

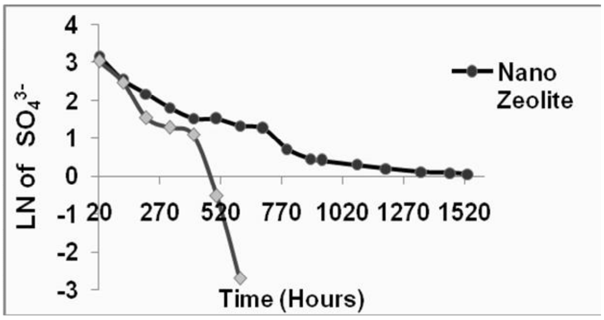

Fig. 3. Kinetics of sulphate release from nano-zeolite and calcium sulphate

Conclusion

The sorption and desorption of nutrients showed that the nano-zeolite adsorbed higher amount of nutrients and released in slow and steady rate thereby improving the use efficiency without associates environmental harm.

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