Microporous and Mesoporous Materials 232 (2016) 174–183

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Synthesis and characterization of zeolite based nano–composite: An environment friendly slow release fertilizer

Ambreen Lateef [a], Rabia Nazir [b, *], Nadia Jamil [a], Shahzad Alam [c], Raza Shah [d], Muhammad Naeem Khan [b], Murtaza Saleem [e]

[a] College of Earth and Environmental Sciences, University of the Punjab, Lahore 54500, Pakistan
[b] Applied Chemistry Research Centre, Pakistan Council of Scientific and Industrial Research Laboratories Complex, Ferozepur Road, Lahore 54000, Pakistan
[c] Pakistan Council of Scientific and Industrial Research Laboratories Complex, G-5/2 Islamabad, Pakistan
[d] H.E.J Research Institute of Chemistry, International Center for Chemical and Biological Sciences, University of Karachi, Karachi 75270, Pakistan
[e] Department of Physics, School of Science and Engineering, Lahore University of Management Sciences, Lahore 54792, Pakistan

ARTICLE INFO

Article history:
Received 5 March 2016
Received in revised form
8 May 2016
Accepted 12 June 2016
Available online 14 June 2016

Keywords:
Nano-zeolite
Zeolite based nano-composite
Slow release fertilizer
Macro and micro-nutrients

ABSTRACT

The research deals with assessing the feasibility of using nano-zeolite as support material for the provision of nine out of thirteen primary, secondary and micro-nutrients on slow release basis. The nano-zeolite (NZ) and nano-composite (ZNC), synthesized using simple chemical approach, were characterized by different techniques including FT-IR, powder XRD, *SEM/EDX*, AFM and TGA/DSC. Physical characterization was also performed by using standard methods. The lab studies showed that there is considerable increase in water retention capacity, water absorbency, equilibrium water content and swelling ratio of ZNC as compared to the NZ which is favorable for maintaining water level in the soil. The nano-composite prepared is safe to use as compared to conventional fertilizers as indicated by salt index value. Nutrients slow release studies carried out in water and soil confirmed the long term availability of all the doped nutrients to the plant over the full crop cultivation period that is suitable for promoting germination, growth, flowering and fruiting. Hence, the results obtained showed that the prepared nano-composite materials can be safely used as environment friendly fertilizer.

1. Introduction

Agriculture practices are very important for people all over the world for providing food but unfortunately these methods are facing several international challenges now days. One such challenge is massive increase in the population which had put enormous burden on the agronomic productions that need to be enhanced with same limited resources of land and water. This resulted in significant rise in fertilizers' usage to enhance soil health that can expedite fast increase in yield per hectare [1]. However, this uncontrolled use of fertilizers had not only caused decline in land quality but owing to their high solubility which results in 40–75% leaching losses, they contribute less towards plant growth and more towards environmental issues [1–3] which directly or indirectly lead to various health concerns [4]. Furthermore, this incurs in huge wastage of fertilizers accounting for economic loses. All these issues together can put enormous financial burden on the society which is not only a matter of serious concern for developing countries which are striving for survival but also for developed countries in attaining sustainability. Therefore, there is a dire need to change agronomic practices by designing new environmental friendly fertilizers that can also enhance crop yield by facilitating maximum nutrient uptake.

Application of nanotechnology in this area can help in promoting sustainable agriculture by provision of slow or controlled release fertilizers, herbicides and pesticides [5–7]. Several researches have been carried out in this context which dealt with the development of nanoparticles or nano-composites to facilitate

Abbreviations: AFM, Atomic Force Microscopy; DSC, Differential Scanning Calorimetry; EDX, Energy-dispersive X-ray Spectroscopy; EWC, Equilibrium Water Content; FTIR, Fourier Transforms Infrared Spectroscopy; HDTMA, Hexa Decyl Trimethyl Ammonium; SI, Salt Index; SR, Swelling Ratio; SRF, Slow Release Fertilizer; SEM, Scanning Electron Microscope; SMZ, Surface Modified Zeolite; TGA, Thermal Gravimetric Analysis; TDS, Total Dissolved Solids; TH, Total Hardness; WR, Water Retention; WA, Water Absorbance; XRD, X-ray Diffraction; ZNC, Zeolite Based Nano-composite.

* Corresponding author.
E-mail address: rabiapcsir@yahoo.com (R. Nazir).

http://dx.doi.org/10.1016/j.micromeso.2016.06.020
1387-1811/© 2016 Published by Elsevier Inc.

plant growth either by direct uptake or by slow release of nutrients [8]. Total of 16 nutrients are required by the plants out of which 13 are usually taken up from the soil. Nano-fertilizers have helped in provision of these essential nutrients to the soil on continues basis by slow release. This gradual release promotes enhanced delivery of nutrients to the plants that further accelerates early germination, fast growth and high nutritional level [9].

Zeolite, in general, is known to support crop cultivation by improving soil condition through enhancing nutrients and water utilization efficacy, biological activity and fertility and minimizing ammonia volatilization and soil salinity [10–14]. Additional advantage of zeolite is that it enhances the nutrient retention capacity of soil which leads to increased availability of nutrients to the plants for longer period of time because of its slow disintegration and decomposition rate in soil [5]. Considering all these advantages of zeolite, the material has recently gained much attention and is being used to deliver fertilizer to the plants at slow rate after some structural modifications [15–19]. Not much of the work is cited on applicability of nano-zeolite as slow-release fertilizer, the few studies that have been carried out are conducted by Subramanian et al. [20,21]. They showed that these nano-zeolites release nutrients over a much longer period of time when compared with conventional fertilizers thereby reducing nutrients' leaching losses considerably [22]. High pore density, enhanced surface area and anion exchange capacity of nano-zeolites favors the retention of anions [20,23,24].

The only drawback associated with the use of these fertilizers is related with their incapability in loading cations in considerable amounts on to its porous structure. For this purpose various structural modifications were performed to increase both cation and anion uptake capacities either by use of surfactants [21,22] or by prolonged thermal treatment [20]. These additional treatments not only add up to the cost of fertilizers but also the use of surfactants put extra burden on the environment [25,26].

Therefore, the need is to design simple and cost-effective ways for the synthesis of nano-zeolite that can enhance the nutrient uptake capacity in addition to reducing the environmental impacts caused by use of conventional and environmental hazardous materials. The current research is henceforth aimed to develop simple methodology for synthesis of nano-composite of zeolite that not only facilitates the enhancement in ion exchange capacity but also acts as a material that can act as a continues source of both macro and micro-nutrients throughout the period of crop growth.

2. Experimental

2.1. Chemicals

All chemicals used in the study are of analytical grade. Sodium phosphate monobasic dihydrate ($NaH_2PO_4 \cdot 2H_2O$), magnesium sulphate heptahydrate ($MgSO_4 \cdot 7H_2O$), aluminum sulphate heptahydrate ($Al_2(SO_4)_3 \cdot 7H_2O$), and ethylene glycol ($C_2H_6O_2$) were taken from Merck, Germany. Sodium hydroxide (NaOH), calcium phosphate ($Ca_3(PO_4)_2$), zinc sulphate heptahydrate ($ZnSO_4 \cdot 7H_2O$) potassium chloride (KCl) and sodium silicate solution (Na_2SiO_3) were procured from DAEJUNG while sodium chloride (NaCl), sodium nitrate ($NaNO_3$), ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), nitric acid (HNO_3) and hydrochloric acid (HCl) were supplied by Sigma-Aldrich.

2.2. Synthesis of zeolite nano-composite (ZNC)

Two-step approach was adopted to synthesize ZNC; in first step zeolite was prepared that was impregnated with nutrients in second step.

2.2.1. Synthesis of nano-zeolite (NZ)

Nano-zeolite (NZ) was synthesized by simple co-precipitation method [27]. Sodium silicate solution (220 g/300 ml distilled water) and ethylene glycol (25 ml) were taken in a three necked round bottom flask fitted with reflux condenser and quick fit dropping funnels. The contents were stirred for 30 min while maintaining the temperature at 50–60 °C to get homogenous mixture. To this aluminum sulphate (78.7 g/250 ml) and sodium hydroxide (30 g/250 ml) solutions were added drop-wise along with stirring and heating (50–60 °C). When dropping was completed pH was adjusted to neutral using 1 N HCl followed by filtration, oven drying at 105 °C and annealing at 650 °C to result in grey colored zeolite.

2.2.2. Synthesis of zeolite nano-composite (ZNC)

The zeolite based nano-composite (ZNC) was synthesized by simple impregnation of nutrients in NZ. To the suspension of NZ in distilled water (200 g/l) 5% solution of each of macro (N, P, K, Ca, Mg, S) and micro-nutrients (Fe, Zn, Cu) in the form of their salts ($NaH_2PO_4 \cdot 2H_2O$, $MgSO_4 \cdot 7H_2O$, $Ca_3(PO_4)_2$, $ZnSO_4 \cdot 7H_2O$, KCl, $NaNO_3$ and $FeCl_2 \cdot 4H_2O$) were added and allowed to stir for 3 h to attain maximum impregnation of these nutrients into NZ. The resulting suspension was vacuum filtered, oven dried (105 °C) and fine grinded in blender at 12,000 rpm. The prepared zeolite was stored in air-tight container till further use.

2.3. Characterization

2.3.1. Physical properties

The physical properties including pH (ASTM D 4959-00), conductivity (ASTM D1125-14), moisture content (ASTM 4643-08), bulk and tap densities (ASTM D2854-70), methylene blue (MB) value (ASTM C1777-15), ash content (ASTM D2866-70) and cation exchange (CEC) and anion exchange (AEC) capacities of NZ and ZNC were determined by standard methods [28].

2.3.2. Fourier transform infrared spectroscopy (FT-IR)

The material characterization was done using FT-IR Thermo Nicolet spectrometer series by scanning the sample pallet made with KBr in the range of 4000–400 cm^{-1}.

2.3.3. Powder X-ray diffraction (XRD)

Powder XRD analysis was carried out using PANanalytical X'pert pro diffractometer by a Philips X-ray generator. Diffraction data was acquired by exposing powder samples to Cu-Kα X-rays radiation, which has a characteristics wavelength of 1.5418 A°. X-rays were generated from a Cu anode supplied with voltage of 40 kV and a current of 40 mA. The data were collected over a range of 20–80°2θ with a step size of 0.05 and nominal time per step is 0.5 s.

2.3.4. Scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX)

Gold coated pallets of the samples were used to acquire the SEM images on Nova NanoSEM 450 while powder samples spread on carbon tape were used to determine the elemental composition using EDX, Nova 450 at 5.00 kV.

2.3.5. Atomic force microscopy (AFM)

The topographic images of atomic force microscopy were recorded with AFM 5500 (Agilant, USA). Silicon nitride probe with a triangle soft cantilever (Veeco, model MLTC-AUHM) having a nominal value of the spring constant of 0.01 and 0.1 N/m used in the non-contact topography measurements. Ethanolic solution of sample (100 μg/ml) was vortexed for 1 min followed by sonication (KQ 500-DE) for 30 min. From this 10 μl solution was taken and