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Research paper

Urea–hydroxyapatite-montmorillonite nanohybrid composites as slow release nitrogen compositions

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ABSTRACT

Nanohybrid composite was developed by the encapsulation of urea modified hydroxyapatite nanoparticles into the nanolayers of montmorillonite. The nanohybrid composites were synthesized by two approaches; solution phase synthesis and liquid assisted grinding techniques and were tested for their slow release nitrogen in soil. The characterization results revealed the successful realization of a nanohybrid containing urea modified hydroxyapatite nanoparticles encapsulated in montmorillonite. The release behavior of urea in different pH values indicated a slow and sustained release of nitrogen. The rate of release of N was significantly lower in the nanohybrid composite prepared using solvent assisted grinding techniques. Pot trials conducted using *Oryza sativa* (rice) demonstrated a significant yield enhancement with the novel plant nutrient system. Montmorillonite nanohybrid composite thus prepared can be used as an environmentally friendly fertilizer formulation which could be extended to solve one of the major problems faced in the global fertilization of low nitrogen use efficiency in agriculture.

1. Introduction

With the world population surpassing 7.5 billion in 2017 (PRB, 2017), "the neglect by governments and international agencies of agriculture relevant to the poor, the current worldwide economic crisis, and the significant increase of food prices have made close to a billion people, mostly in the developing world suffer due to malnutrition" (Karunaratne et al., 2012). Increasing the quantum of crop yields coupled with decreasing the adverse environmental effects of using large quantities of nitrogen fertilizer is vital in achieving a sustainable solution to the future food demands of the planet. From the standpoint of chemical fertilizers used in agriculture, they have indeed provided the basis for predictable and consistent crop yields over the past 150 years. However, the nutrient use efficiency (NUE) by plants has been estimated to be very poor, particularly in relation to N, P and K. For example, in comparison to what is applied to soil, between 50 and 70% of N is lost due to leaching, volatalisation in the form of ammonia and nitrogen oxide and long term incorporation into soil organic matter (Monreal et al., 1986). Therefore, currently, there is an urgent need to improve the NUE. In this regard, scientists have predicted that nanotechnology approaches may solve most of the problems related to agriculture and NUE within the next few decades. Owing to the high surface area to volume ratio of nanoparticles, nanofertilizers are expected to enable the uptake of fertilizer by plants on demand, in a slow and sustained manner (DeRosa et al., 2010). Such paradigm shift in fertilizer practices would be more efficient, lead to cost savings and less environmental damage (Kottegoda et al., 2012).

Functional hybrid nanomaterials have recently received substantial scientific interest for their promising performances in nanotechnological applications. A combination of more than one nanocomponent into a hybrid structure gives rise to multifunctional properties due to synergistic effects, arising from particle-particle interactions (Banin,

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2007; Tran and Nguyen, 2013). Morphology of the hybrid nanostructures is a critical factor that determines the performance of the final composite (Glotzer, 2012; Perera et al., 2015). In order to achieve these synergistic and multifunctional properties, the shape-controlled synthesis through controlling heterogeneous nucleation-growth kinetics during the synthesis has been explored. Wet-chemistry methods, such as seed-mediated growth, ion exchange, deposition, thermal decomposition, hydro thermal process used to synthesize single nanoparticles have been extended to the hybrid nanostructures. Pillaring and/or encapsulation of layered compounds with nanoparticles or molecular clusters have attracted more attention in this regard (Tran and Nguyen, 2013). In particular, the semiconductor nano-sol pillars based on clays and TiO_2 nanoparticles have been reported for their excellent photocatalytic activity (Chen et al., 2011).

We have previously reported the surface modification of HA nanoparticles with urea and its encapsulation in wood chips (Kottegoda et al., 2011). Further, advanced studies on urea-HA nanohybrids and bioavailability studies were also reported (Gunaratne et al., 2016; Kottegoda et al., 2013a, 2013b, 2014a, 2017, 2014c). The current study is a realization of the synthesis of an improved nanohybrid composite based on montmorillonite (Mt) and hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ nanoparticles (HA np) encapsulated with the major plant macronutrient urea in a further attempt to mitigate the loss of nitrogen from soil. In this study, urea-HA nanohybrids synthesized as explained by Kottegoda et al., 2017 were further encapsulated into a Mt matrix in order to assist the nutrient use efficiency of the plants by acting as a reservoir for encapsulating the nutrients and supporting the cation balance in soil. Few previous attempts to encapsulate urea into Mt and other layered materials have been reported previously (Kottegoda et al., 2014b; Pereira et al., 2012). In this study attempts are made to synthesize the nanohybrid composite via solvent assisted grinding which involves the use of lower amount of water to compose urea-HA nanohybrids incorporated Mt thus minimizing the energy consumption for drying which leads to facile and low cost preparation of stable and efficient product (Toson et al., 2015).

2. Experimental

2.1. Materials

All reagents and chemicals used in this study were purchased from the Sigma Aldrich Company, USA and were of analytical grade and used without further purification. All aqueous solutions were prepared using distilled water. Mt was purchased from Southern Clay, USA.

2.2. Characterization techniques

Powder X-ray Diffraction patterns (PXRD) of all synthesized samples were recorded using a Bruker D8 Focus X-ray powder diffractometer using Cu Kα radiation ($\lambda = 0.154$ nm) over a 2θ range of 3–65° with a step size of 0.02° and a step time of 1 s.

The particle size and the morphology of the synthesized samples were studied on a HITACHI SU6600 Scanning Electron Microscope (SEM). Samples were coated with a thin layer of Au prior to observation and secondary electron mode was used for imaging. Elemental analysis was carried out using energy dispersive X-ray (EDX) analysis.

Transmission electron microscopic analysis was carried out using JEOL JEM 2100 microscope operating at 200 keV.

The samples were dispersed in methanol using ultra sound sonication for 5 min. The dispersed nanoparticles were loaded on lacey carbon-coated copper grids (300 mesh) and the sample containing grids were dried for 24 h at room temperature prior to observation.

The nature of chemical bonding of the synthesized samples was determined using a Bruker Vertex 80 Fourier Transform Infra-Red Spectrometer (FTIR) in the range from 600 to 4000 cm^{-1} using Attenuated Total Reflectance (ATR) technique.

Nitrogen analysis of the composites and leached samples were analyzed using the Kjeldahl method (Bremner, 1996).

2.3. Synthesis and surface modification of HA np with urea (U-HA)

HA nanoparticles were synthesized and surface modified with urea at a ratio of U:HA (1:1) by an in-situ co-precipitation method described in Kottegoda et al. (Kottegoda et al., 2011).

2.4. Synthesis of U-HA-Mt nanohybrid composite–solution phase synthesis (SPS) method (U-HA-Mt-SPS)

Na-Mt (10 g) was dispersed in distilled water (150 ml). Then, urea modified HA nanoparticle dispersion prepared under ultrasound sonication (30 kHz for 45 min), was added drop wise to the Na-Mt dispersion. The prepared U-HA-Mt nanocomposite was oven dried at 60 °C for 10 h. A similar procedure was used to prepare U-Mt composites for comparison purposes.

2.5. Synthesis of U-HA-Mt nanohybrid composite–liquid assisted grinding (LAG) method (U-HA-Mt-LAG)

U-HA (100 g) synthesized as explained above was mixed with Na-Mt (142 g) and ground in a grinder (13,800 rpm) for 5 min. Water (25 ml) was added to the ground U-HA-Mt solid compound and grinding was continued for further 20 min. The solid composite was oven dried at 60 °C for 30 min. The solid compound was characterized and compared with that received by SPS method.

2.6. Release behavior studies of the U-HA-Mt nanohybrid composite in soil

Soil sample (400 g, pH 5.2) was mixed with 1.8 g of commercial Ceylon tea fertilizer formulation containing urea. This soil sample containing urea was filled into a glass column. Similarly, equal amounts of U-HA-Mt nanohybrid composite prepared by SPS and LAG methods containing equal amount of nitrogen to that of the commercial sample were separately mixed with soil (400 g, pH 5.2) and filled into other glass columns. Next, 180 ml water was added to all soil columns until they reached the soil water saturation point, and maintained the water content approximately constant throughout the period of study. Water (100 ml) was added at four day intervals and allowed to elute through the column at a constant speed. The eluted solutions (100 ml) were collected for nitrogen analysis.

Release (%) is presented according to,

$$\text{Release }(\%) = \frac{\text{Cumulative N content released (mg)}}{\text{Added N content (mg)} + \text{soil (bare) N content (mg)}} \times 100\%$$

2.7. Bioavailability studies of the U-HA-Mt nanohybrid composite

Bioavailability studies of the nanohybrid composites were carried out at the Rice Research and Development Institute of Sri Lanka using *Oryza sativa* (rice) as the model crop. The N, P, K content of a soil unfertilized for 25 years was evaluated prior to use in pot trials. Soil (5 kg) was filled into pots and nanohybrid composite was applied two weeks prior to sowing. Conventional fertilizer composition, N (120 kg/ha), P_2O_5 (40 kg/ha) and K_2O (40 kg/ha) was applied separately according to the recommendations by the Department of Agriculture (DOA), Sri Lanka. A separate controlled experiment was conducted using no externally applied nitrogen nutrient. Each pot contained five plants while six replicates of each treatment were maintained.

The nutrient amounts and application protocols are summarized below.

1. T1–No N, P and K application