



## 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, volatilisation 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<sub>2</sub> 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<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> 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 K $\alpha$  radiation ( $\lambda = 0.154$  nm) over a  $2\theta$  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<sup>-1</sup> 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,

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

### 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<sub>2</sub>O<sub>5</sub> (40 kg/ha) and K<sub>2</sub>O (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

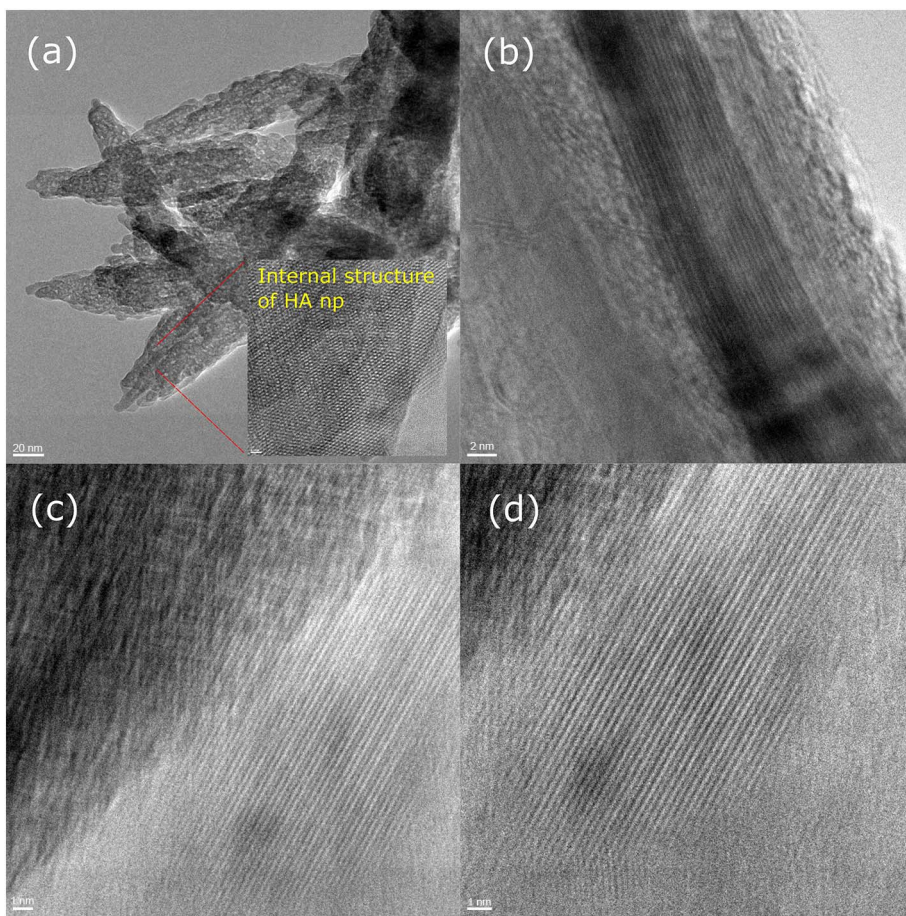


Fig. 1. (a) TEM image of U-HA np and HRTEM image showing the internal structure of the HA np, (b) HRTEM of pure Na-Mt, (c) HRTEM of U-HA-Mt-SPS and (d) HRTEM of U-HA-Mt-LAG.

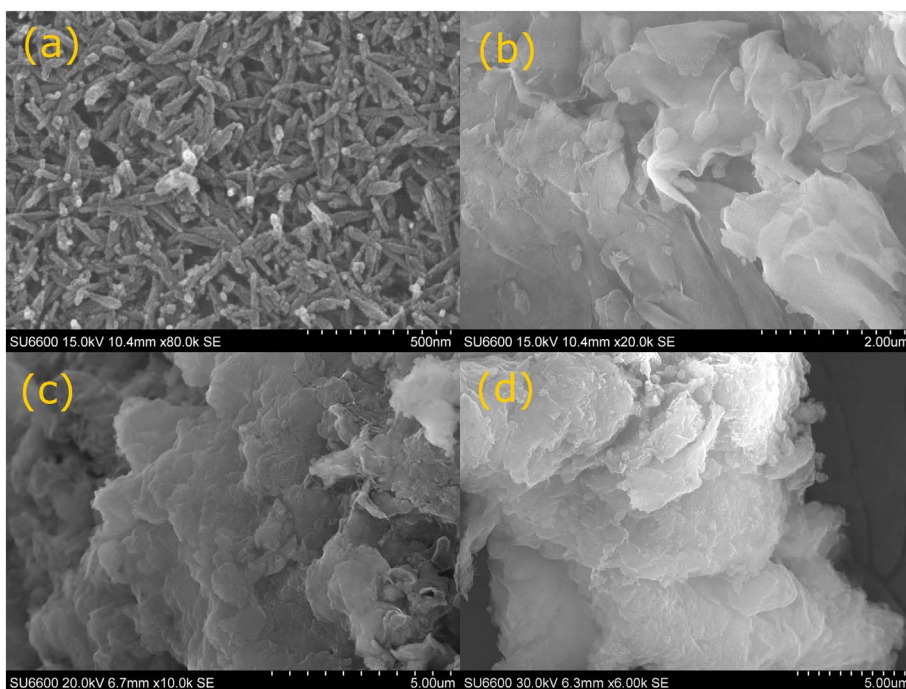


Fig. 2. SEM images of (a) U-HA Np dispersion, (b) Na-Mt, (c) U-HA-Mt-SPS and (d) U-HA-Mt-LAG.

2. T2-N (urea), P (triple superphosphate), and K (muriate of potash) at standard dose described as a basal dressing and three top ups during the period of experiments.
3. T3-U-HA-Mt-SPS nanohybrid composite 50% of the standard dose described as a basal dressing only, all other nutrients were supplied

- as per standards.
4. T4-U-HA-Mt-LAG nanohybrid composite 50% of the standard dose described as a basal dressing only, all other nutrients were supplied as per standards.

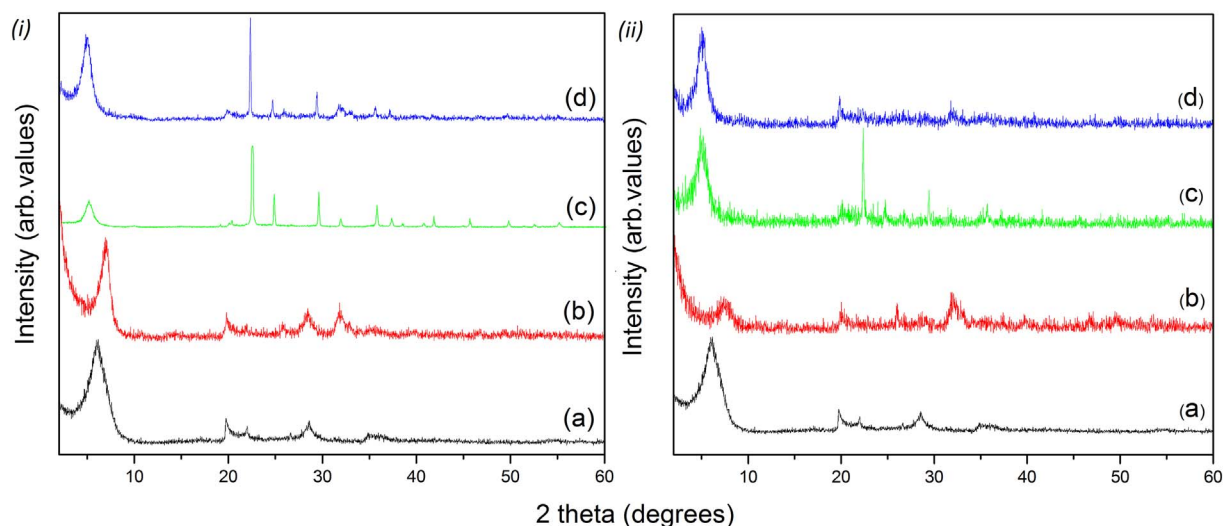


Fig. 3. PXRD patterns of (a) Na-Mt, (b) HA-Mt, (c) U-Mt and (d) U-HA-Mt synthesized using (i) SPS method and (ii) LAG method.

Measurements were made on the tillers per pot, filled grains per pot and grain yields.

### 3. Results and discussion

HA np and U-HA np were characterized as explained by Kottegoda et al., 2011. HA np exhibited a rod-like morphology and hexagonal crystal structure as reported previously (Kottegoda et al., 2017) and confirmed using TEM and HRTEM studies (Fig. 1(a)).

According to HRTEM image (Fig. 1(c) and (d)) there are no areas of phase separation of U-HA and Mt confirming the successful formation of an encapsulated nanocomposite between the two nano matrices Mt and U-HA and can be further confirmed using SEM images (Fig. 2).

U-HA np encapsulated into the Mt matrix via SPS and LAG methods were characterized comparing with Na-Mt (parent clay), U-Mt and HA-Mt composite systems. The PXRD patterns of the Na-Mt, U-Mt, HA-Mt and U-HA-Mt nanohybrid composites prepared by SPS and LAG methods are compared in Fig. 3 (i) and (ii) respectively.

An interlayer spacing of 1.52 nm is obtained for Na-Mt as calculated according to the Bragg's law, referring to the first basal reflection (001) in the PXRD pattern. Introduction of urea, a small organic molecule increased the interlayer spacing of the parent Na-Mt to 1.78 nm. The hydrophilic nature of the interlayer space of Mt allows the easy

migration of small molecules with hydrophilic groups through strong H-bonding thus leading to an expansion in the interlayer distance. Surprisingly, the first basal reflection of Na-Mt is shifted to a higher 2 theta value after encapsulation of HA np leading to a reduction of the interlayer distance to 1.41 nm (Fig. 3 (i)). The shrinking of the interlayer distance can be attributed to the strong interactions between O–H groups of HA np and the surface-active groups present in Mt nanolayers (Kalpana et al., 2008) leading to a grafting interaction on to the edges and surfaces of the Mt layers rather than a pillared composite. However, when U-HA nanohybrid is blended with the Mt structure the interlayer spacing increased to 1.80 nm suggesting a successful encapsulation interactions. This increase in the interlayer region is lower than the size of the U-HA nanohybrid if it was intercalated. Therefore, these observations lead to the conclusion that a hierarchical nanocomposite is obtained through encapsulation and grafting interaction through different binding sites available in Mt. Separate diffraction peaks corresponding to HA np are not observed in both HA-Mt and U-HA-Mt nanohybrid composite materials thus supporting the conclusion of an encapsulated nanohybrid composite rather than two individual solid phases.

A larger interlayer spacing of 1.94 nm is observed for the U-HA-Mt nanohybrid composite prepared by LAG method (Fig. 3 (ii)). Unlike with the SPS method, the absence of diffraction peaks corresponding to

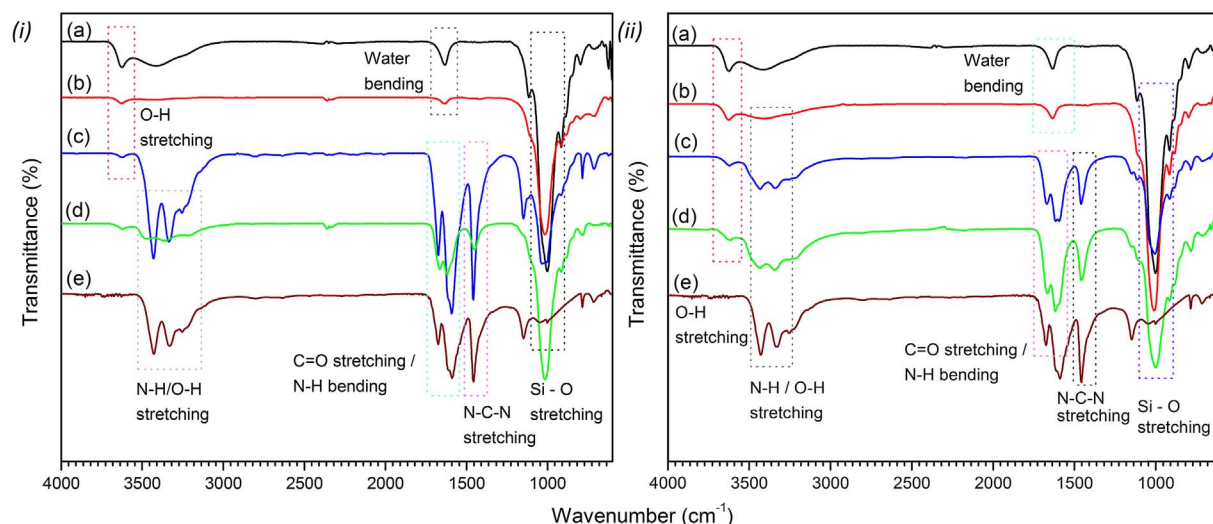


Fig. 4. FTIR spectrum of (a) Na-Mt and (b) HA-Mt, (c) U-Mt (d) U-HA-Mt synthesized using (i) SPS method and (ii) LAG method with (e) Urea.

**Table 1**  
FTIR data for nanohybrids prepared by SPS and LAG methods.

Composition	Wavenumber ( $\text{cm}^{-1}$ )						
	Free O–H stretching	N-H/structural O–H stretching	Carbonyl stretching	N-H bending	Water bending	N-C-N stretching	Si-O stretching
Urea		3482 (s), 3330 (s)	1680 (s)	1625 (s)		1459 (s)	
Na-Mt	3635 (s)	3415 (b)			1630 (s)		1060 (s)
HA-Mt-SPS	3625 (b)				1635 (s)		1016 (s)
U-Mt-SPS	3623 (b)	3432 (s), 3338 (s)	1670 (s)	1592 (s)		1460 (s)	1020 (s)
U-HA-Mt-SPS	3620 (b)	3472 (b), 3319 (b)	1664 (s)	1619 (s)		1450 (s)	1016 (s)
U-HA-Mt-LAG	3619 (b)	3430 (b), 3314 (b)	1669 (s)	1619 (s)		1456 (s)	1000 (s)

(s) – sharp peaks, (b) – broad peaks.

pure urea suggests that the LAG method facilitates an efficient encapsulation of U-HA nanohybrids into the Mt matrix avoiding any crystallization of free urea regions, thus forming a better structural nanohybrid composite. The high shear forces acting on the reactants during grinding facilitate the encapsulation of U-HA np into the Mt matrix leading to a better structural composite than that obtained by SPS method. LAG methods, also eliminate the requirement of large quantities of water needed for efficient and effective reaction between the U-HA np complex and Mt layers while significantly minimizing the longer drying time and high energy required when SPS methods were followed.

According to Fig. 4 (i) and (ii), the FTIR spectra of the U-HA nanoparticles encapsulated into Mt nanolayers displayed peaks due to HA np, urea and Na-Mt confirming the presence of the urea modified HA nanoparticles within the Na-Mt system.

Evidences for the successful encapsulation of the U-HA nanohybrids into the Mt matrix provided by the lower wavenumber shift and broadening of the peaks due to O–H stretching frequency of Mt, metal–oxygen stretching vibrations of Mt and N–H stretching vibrations and bending vibrations of urea and carbonyl stretching vibrations of urea (Table 1).

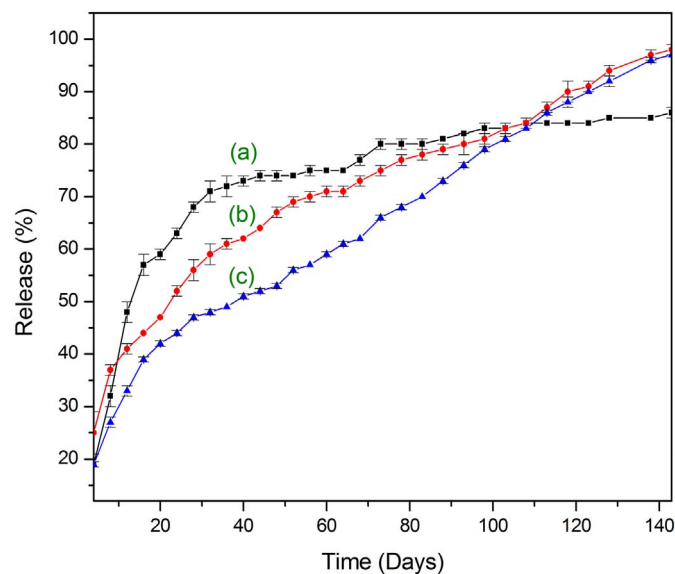
Peak broadening at  $\sim 3600 \text{ cm}^{-1}$  of the parent clay after encapsulation of the urea modified HA nanoparticles, suggests an H-bonding environment within the Mt interlayer spacing while the lower wavenumber shift ( $44 \text{ cm}^{-1}$ ) in silicon–oxygen bond from  $1060 \text{ cm}^{-1}$  to  $1016 \text{ cm}^{-1}$  after intercalation accounts for the electron density changes in the Mt layers as a result of encapsulation of U-HA nanoparticles. Further, the lower wavenumber shift of carbonyl groups from  $1680 \text{ cm}^{-1}$  to  $1670 \text{ cm}^{-1}$  and amino groups from  $3482 \text{ cm}^{-1}$  to  $3472 \text{ cm}^{-1}$  for the asymmetric vibrations and  $3330 \text{ cm}^{-1}$  to  $3319 \text{ cm}^{-1}$  for symmetric vibrations of free urea molecules after encapsulation into HA np from one end and Mt from the other end confirm the presence of strong interactions of urea with HA nps and Mt. Furthermore, the structural O–H stretching vibrations overlapped with the N–H stretching vibrations leading to a broadening and a peak shift to a lower wavenumber. FTIR patterns of the nanocomposites prepared using the LAG method display a similar trend in peak shifting and broadening of the stretching frequencies of the major functional groups discussed for the SPS method. However, the shift in Si–O stretching frequency was by 60 wavenumbers suggesting more strong interactions between two nanohybrids corroborating the results obtained by the PXRD characterization.

N release data of the nanohybrid composites are shown in Fig. 5.

Slow release behavior of nitrogen was shown by the nanocomposite based on U-HA–Mt-SPS and gradual release behavior can be clearly identified with the increase of cumulative nitrogen content up to the 60th day in a slow manner, which is in agreement with a typical slow release profile presented by cumulative release vs. time in the literature (Pereira et al., 2012). The composite prepared by the LAG method showed a similar release pattern, however, the release % of nitrogen was lower than that resulting from the nanohybrid composite prepared by SPS method. Here, as observed from PXRD analysis, the nutrients,

particularly urea, is more tightly bound to two nanohybrids compared to that prepared by the SPS method. Thus, the composite is expected to behave in a slower and a more sustained manner in releasing nutrients leading to a very effective and efficient slow release fertilizer composition opening up new opportunities for efficient fertilizer practices within the next few decades. In this composite, a significant amount of nitrogen release was observed up to the 140th day. In comparison, commercial fertilizer composition containing pure urea as the N source had released almost 80% of N within 10 days and release of nitrogen had stopped after the 30th day. At the 60th day, in the commercial fertilizer, about 90% of N had been released out while the Mt based nanocomposite had released only about 65%.

U-HA np encapsulated into Mt nanocomposite are expected to show unique slow release behavior which is distinctly different from that of free urea when it is broadcasted over the soil surface as a fertilizer. U-HA np are located within Mt particles bonded to the active sites on the Mt layers while some of urea molecules are present in the interlayer space of Mt. Therefore, these urea molecules could be protected against



**Fig. 5.** N release behavior of (a) pure urea, (b) U-HA-Mt-SPS nanohybrid and (c) U-HA-Mt-LAG nanohybrid.

**Table 2**  
Diffusion exponent 'n', gel characteristic constant k and correlation coefficient r for the release of N at different pH.

pH of the N release medium	K	n	r	Diffusion mechanism
7.0	0.26	0.69	0.953	Non-Fickian
5.2	5.87	0.34	0.99	Non-Fickian
4.2	1.09	0.60	0.951	Non-Fickian

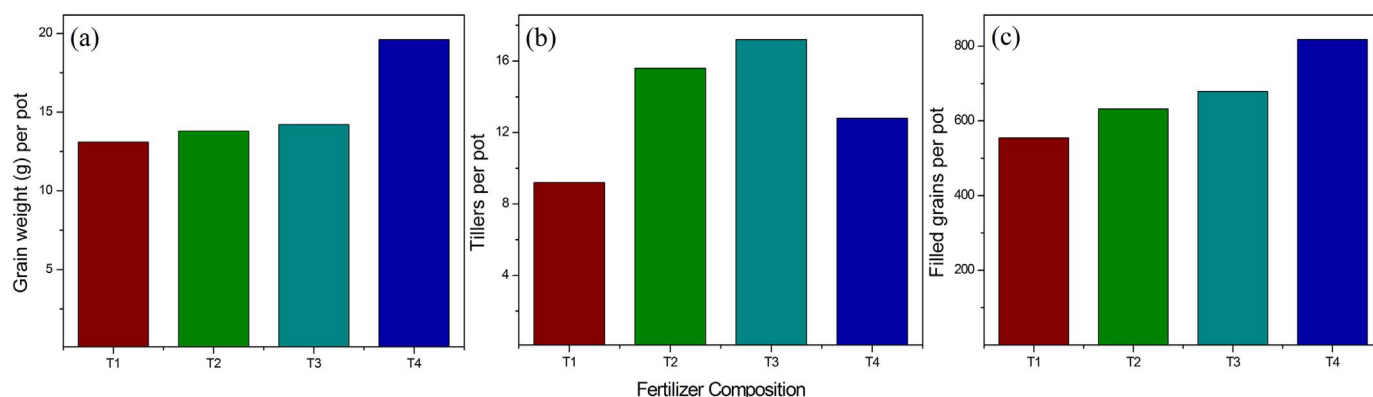


Fig. 6. (a) Grain yield, (b) tillers per pot and (c) filled grains per pot for the treatments T1 – T4.

decomposition by photochemical, thermal, enzymatic, and other catalytic activities of soils unlike free urea molecules on the surface of soil particles. When U-HA np encapsulated Mt composite is in contact with soil water, it adsorbs water and urea molecules are slowly transferred into the soil solution by diffusion. Further, when urea molecules are hydrolyzed to ammonia/ammonium ions, Mt can quickly adsorb the resultant ammonium ions through physical and chemical interactions due to its very high affinity towards intercalation of ammonium ions among all the cations. Therefore, Mt is expected to play an essential role in releasing nitrogen in a slow and sustained manner while suppressing emission of ammonia.

The diffusion mechanism of the urea molecules from nanohybrid composite can be explained by Fickian, Non-Fickian and Case 2 diffusion models (depending on whether the release is through swelling mode, diffusion mode or whether there is a shift from initial swelling mode to diffusion control mode when contacted with moisture, respectively) which have been developed to explain the release behavior of swelling clays (Pereira et al., 2012). According to this mathematical model, the diffusion exponent is determined using the equation,

$$M_t/M_0 = Kt^n$$

Where  $M_t$  is the amount of material released at time  $t$ ,  $M_0$  is the total amount of material added,  $k$  is the rate constant and  $n$  is the diffusion exponent related to the diffusion mechanism. For normal Fickian Case 2 and non-Fickian diffusion value of  $n$  is 0.5, 1 and between 0–0.5 and 0.5–1, respectively. In addition, when the diffusion exponent increases to a value close to 1, it reveals a change in the release mechanism from diffusion controlled mode to swelling controlled mode.

In all formulations, nanohybrid composites show non-Fickian diffusion as given in the Table 2. Non Fickian or anomalous diffusions occur when the diffusion and relaxation rate of the composite are comparable with each other.

The bioavailability testing carried out using *Oryza sativa* (Rice) at the Rice Research and Development Institute of Sri Lanka revealed that a significant yield improvement was observed when nanohybrid composite was used, at 50% of the recommended level as the N source compared to traditional N formulation (Fig. 6).

#### 4. Conclusion

In conclusion, U-HA-Mt nanohybrid composites which are structurally and functionally valuable systems for slow and sustained release of urea into soil have been synthesized. Based on the encouraging results of field trials using *O. sativa* (rice), these Mt nanohybrid composites have the potential of becoming the next generation nitrogen fertilizer systems, where both a higher crop yield and saving of urea may be realized.

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