

Urea modified Calcium Carbonate Nanohybrids as a Next Generation Fertilizer

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Abstract—With increasing world population, sustaining food security of people has become a daunting challenge. Scientists have explored various pathways to feed the global population. One way is the development of efficient nutrient and pest control systems together with improved crop varieties. Most of the conventional fertilizer systems in practice have not met the plant nutrient requirements basically due to the low Nitrogen Use Efficiency (NUE) of plants. There had been many attempts to develop efficient fertilizer systems particularly to supply nitrogen, which is the major nutrient needed for plant growth. Urea, being an excellent candidate for nitrogen fertilizer, it's efficient and targeted delivery is a must. This research focuses on the synthesis of scalable, cost-effective and efficient nitrogen fertilizer, which retards the solubility of nitrogen at a minimum of 5 times compared to pure urea. Being a bioinspired material, calcium carbonate (CC) renders added advantages of biocompatibility and non-toxicity. Urea-CC nanohybrid was synthesized using an in-situ rapid carbonation method which resulted in cubic plate-like nanoparticles which are stacked together to form pine cone-like structures. The Fourier transform infrared spectroscopic data provides conclusive evidence for bonding interactions of urea with CC nanoparticles giving a platform for controlled release properties of urea. Crystallographic data of nanohybrids were obtained from powder X-ray diffraction. Nitrogen release behaviour of the novel nanohybrids exhibited controlled release properties over pure urea demonstrating that the urea modified CC nanocomposites introduced herein have the potential to replace the conventional fertilizer systems to sustain future food security.

Keywords— calcium carbonate, urea, nanohybrid

I. INTRODUCTION

Efficient supply of fertilizers and agrochemicals is the major factor that governs food security. Currently, scientists are more focused on developing efficient and cost effective plant nutrient systems together with improved crop varieties and agrochemicals. Plants

basically fulfil the nutrient requirements needed for the growth by absorbing nutrients from soil. But, the bioavailability of macronutrients (NPK) in soil does not meet the requirement for the sustained growth of plants. Therefore, this gap has to be fulfilled externally through fertilizers (Kottegoda Nilwala *et al.*, 2011).

Nitrogen being the key nutrient in food and the biomass, it's the paramount element needed for plants. Nitrogen fertilizers play a monetary significance since 50–70% of applied nitrogen to the soil by conventional fertilizers are wasted without used by plants. Mainly leaching of nitrates, releasing of nitrogen oxides and gaseous ammonia into atmosphere and incorporation of mineral nitrogen by soil microorganisms has been led to poor nitrogen use efficiency (NUE) by crops (Derosa *et al.*, 2010; Kottegoda *et al.*, 2011). Today there's an increasing attention towards combination of nanotechnology based strategies with conventional fertilizer formulations to develop controlled release fertilizer systems to increase NUE in plants.

Urea being an excellent candidate for nitrogen fertilizers, many different fertilizer nanocomposites has been invented by incorporating urea into different matrices. Calcium carbonate is a commercially important material which carries broad significant applications due to its biocompatibility and non-toxicity (Declat, Reyes and Suárez, 2016). There's no any available literature showing incorporation of calcium carbonate nanoparticles into nitrogen fertilizer systems to increase the NUE. Cost effectiveness and efficacy is a matter of consideration when it comes to commercialization of many products. Here, it is focused on synthesizing the nanohybrid through a bottom-up process which basically ensures stringent control on resultant particle size thereby the characteristics. This research basically focuses on synthesis of novel urea modified calcium carbonate nanohybrid, which can be synthesized using low cost starting materials yet providing controlled and targeted delivery of nitrogen.

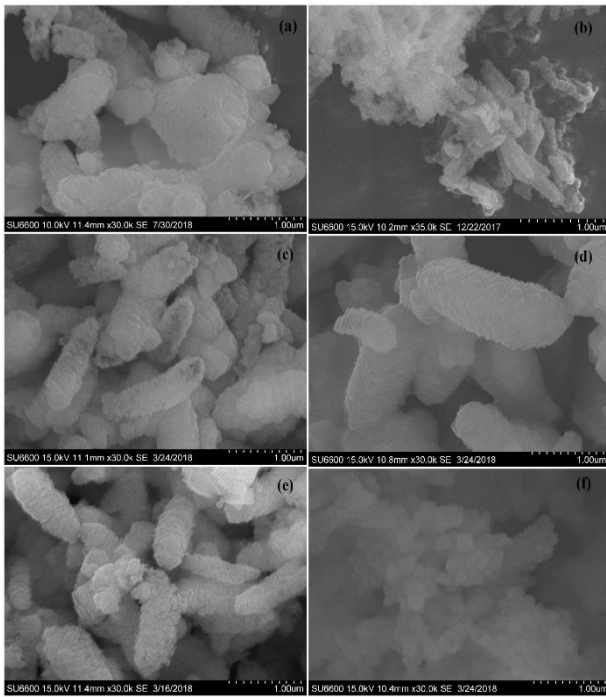


Figure 1. SEM images of synthesized (a) pure CC, (b) 0.5-1 urea-CC composite, (c) 1-1 urea-CC composite, (d) 2-1 urea-CC composite, (e) 4-1 urea-CC composite, and (f) 6-1 urea-CC composite

II. METHODOLOGY

Urea modified CaCO_3 (Urea-CC) nanoparticles were synthesized using one step *in-situ* rapid carbonation method. Urea-CC nanohybrids were prepared in 5 different ratios 0.5:1, 1:1, 2:1, 4:1 and 6:1 respectively. For the preparation of Urea-CC 1:1 composite, 5.0 g of

urea was added to a solution of $\text{Ca}(\text{OH})_2$ (0.2 M, 250.0 cm^3) and stirred (800 rpm) for an hour. The pH of the solution was measured and CO_2 gas was then bubbled at a flow rate of 475 cm^3/s for two minutes until the pH reaches 7. The mixture was stirred vigorously under mechanical agitation (800 rpm) for another two hours and the product was spray dried to obtain a fine powder. Here it was assumed that, higher carbonation rate increases mass transfer from gaseous CO_2 phase to liquid phase forming carbonate ions. Those carbonate ions immediately react with calcium ions resulting multiple CaCO_3 nucleation sites, which are further restricted to grow in size due to the presence of urea medium.

III. RESULTS

According to scanning electron microscopy (SEM) analysis, a significant morphological change between pure calcium carbonate (CC) and urea modified CC was not observed for the composites but the particle size has changed with the loading of urea (Figure 1). Pure CC was observed with the particles having dimensions of 500 nm. With the introduction of urea, cubic plate-like particles with a size distribution of 50-100 nm was observed for the 0.5:1 urea-CC nanocomposite. Interestingly, it was further observed that those cubic plates are stacked together to form elongated rod structures. While increasing the urea amount, the cubic shape was well emerged and those cubed particles have stacked together to form larger pine corn like structures.

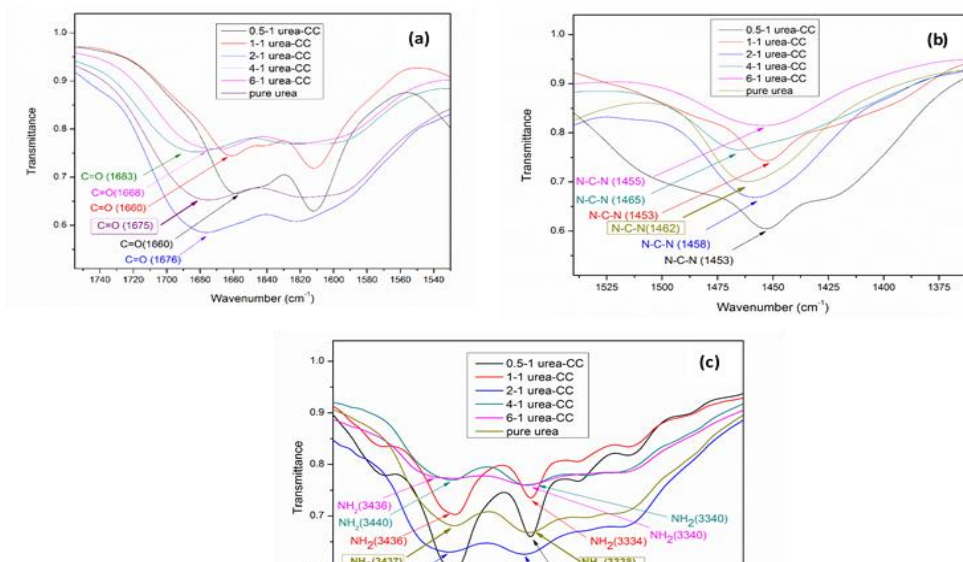


Figure 2. FT-IR spectra for (a) carbonyl stretching region, (b) N-C-N stretching region, and (c) amine stretching region

The available nitrogen contents of all synthesized composites obtained from Kjeldahl analysis were well matched with theoretical values, suggesting that spray drying has not altered homogeneity of composites. In order to understand the bonding interactions between CC nanoparticles and urea, FT-IR spectra of pure urea and composites were compared (Figure 2). The appearance of peak shifts in amine, carbonyl and N-C-N regions to lower wavenumbers provided conclusive evidence for weak interactions between urea and CC (Samavini *et al.*, 2018 ; Kottegoda *et al.*, 2014).

The carbonyl stretching frequency of pure urea appears at 1675 cm^{-1} while the corresponding peak for urea modified CC was appeared at 1660 cm^{-1} , 1660 cm^{-1} , 1668 cm^{-1} for 0.5:1 urea-CC, 1:1 urea-CC, and 6:1 urea-CC respectively. This observation indicates that the C=O electron density has been affected by the interaction of urea with CC. While in the 2:1 and 4:1 urea-CC composites, the corresponding carbonyl peak was appeared at 1676 cm^{-1} and 1683 cm^{-1} respectively indicating that the carbonyl region has not been affected by the urea modification. This further suggests that there is a possibility of having unbound urea molecules when the urea to CC ratio is increased which tend to release at early stages during fertilization. As shown in the Figure 2, the N-H stretching frequency of pure urea appeared as a doublet at 3437 cm^{-1} and 3338 cm^{-1} due to the symmetric and asymmetric stretching of N-H bond and a peak shift to a lower wavenumber of those vibrations indicates that the interactions are occurred through the amine region when CC is modified with urea. In addition, as a credence to above observations a noticeable shift was appeared in N-C-N region. The N-C-N stretching frequency for pure urea was observed at 1462 cm^{-1} where it was shifted to 1453 cm^{-1} , 1453 cm^{-1} , 1458 cm^{-1} , and 1455 cm^{-1} in 0.5:1, 1:1, 2:1, and 6:1 urea-CC composites respectively. However, in 4:1 urea-CC composite N-C-N stretching vibration was observed at 1465 cm^{-1} indicates the presence of free urea molecules which are not bonded to CC.

The powder x-ray diffraction (PXRD) patterns were obtained to represent crystallographic data of urea-CC composites which are shown in Figures 3. According to the obtained powder diffraction data it was concluded that all the composites formed during the rapid carbonation method are in calcite form and no other metastable crystalline forms of CaCO_3 such as aragonite, vaterite were not identified. Synthesized CC shows characteristic peaks in the range of 2θ , $20\text{-}60^\circ$ for (012), (104), (006), (110), (113), (202), (018), (016), and (122) planes confirming the formation of calcite phase. No impurity peaks were observed other than the peaks due to the urea indicating the composites have been synthesized in the form of high purity calcite.

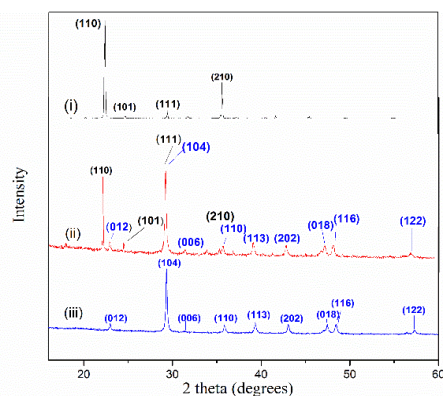


Figure 3. Comparison of PXRD patterns of (i) pure urea, (ii) 0.5-1 (urea-CC) nanohybrid, and (iii) pure CC

Release behavior of urea in water for each sample was conducted according to an accelerated water release test available in literature (Kottegoda *et al.*, 2017). From each sample, nitrogen amounts containing 0.46 g were placed in the soil column and distilled water was pumped from the bottom of the chamber at flow rate of 3.30 mL/min continuously. Eluents were collected at each 20 s intervals and immediately analyzed using FTIR spectroscopy for the appearance of N-C-N stretching.

According to the rapid release test, the different nitrogen amounts released compared to pure urea. Dissolution of pure urea in water shows a rapid release within 140 s and nitrogen amount of 91% (0.42 g out of 0.46 g) has been released during that time period (Figure 4). All other synthesized composites of 0.5:1, 1:1, and 2:1 urea-CC showed a slow, controlled release behavior respect to pure urea except 6:1 and 4:1 urea-CC composites.

Furthermore, nitrogen amounts of 18% (or 0.084 g), 10% (or 0.044 g), and 15% (or 0.067 g) has been released within 140s for 0.5:1, 1:1, and 2:1 urea-CC composites respectively. This indicates that, these composites own it's ability to retard nitrogen solubility 5 times compared to urea. According to the rapid water release test, urea modified CC composites of 6:1 and 4:1 urea-CC did not show a controlled release behavior compared to pure urea.

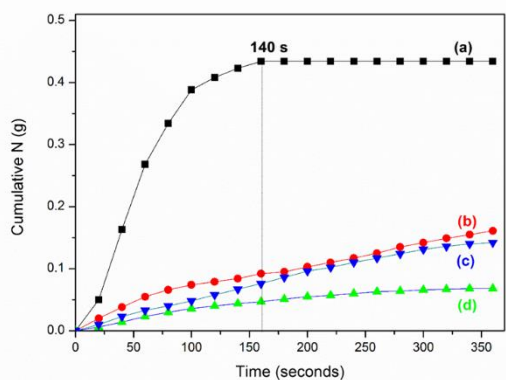


Figure 4. Comparison of release behavior of (a) urea, (b) 0.5:1 urea-CC composite, (c) 2:1 urea-CC composite, and (d) 1:1 urea-CC composite in water.

However, the actual release behavior of the urea-CC composites in soil would be slightly slower than the observed rates since an accelerated water flow was maintained in the experimental setup in the rapid water release test whereas in conventional applications fertilizer would be exposed to low water contents which may further reduce the nutrient content.

IV. CONCLUSION

The rapid carbonation method that we have introduced herein for synthesizing urea modified CC is a scalable, low energy consuming, and cost effective method which resulted in novel nanofertilizer system.

In summary, it can be concluded that urea modified CC formulations of 0.5:1, 1:1, and 2:1 urea-CC composites comparatively shows controlled release behaviour over conventional nitrogen fertilizers systems, leading to another novel controlled release fertilizer system while providing an answer to reduce the tonnage of daily fertilizer usage.

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REFERENCES

- Declat, A., Reyes, E. and Suárez, O. M. (2016) 'Calcium carbonate precipitation: A review of the carbonate crystallization process and applications in bioinspired composites', *Reviews on Advanced Materials Science*, 44(1), pp. 87–107.
- Derosa, M. C. *et al.* (2010) 'Nanotechnology in fertilizers', *Nature Nanotechnology*. Nature Publishing Group, 5(2), p. 91.
- Kottegoda, N. *et al.* (2014) 'Composition and method for sustained release of agricultural macronutrients', (January), pp. 1–7. Available at: <http://www.google.com/patents/US8696784>.

Kottegoda, N. *et al.* (2017) 'Urea-Hydroxyapatite Nanohybrids for Slow Release of Nitrogen', *ACS Nano*, 11(2), pp. 1214–1221.

Kottegoda Nilwala *et al.* (2011) 'A Green Slow Release Fertilizer Composition Based on Urea Modified Hydroxyapatite Nanoparticles Encapsulated Wood', *Current Science*, 101(2), pp. 73–78.

Samavini, R. *et al.* (2018) 'Effect of Citric Acid Surface Modification on Solubility of Hydroxyapatite Nanoparticles', *Journal of Agricultural and Food Chemistry*, 66(13), pp. 3330–3337..