ENHANCING THE SOIL HEALTH AND NUTRIENT EFFICIENCY USING CONTROL RELEASE UREA FERTILIZER COATED WITH BIOCOMPATIBLE NANOMATERIALS

Project Reference No.: 48S_MSC_0235

College : St. Joseph's University, Bengaluru
Branch : Department of Chemistry
Guide(s) : Dr. Nalini G Sundaram
Student(s): Mr. V Sai Subramanian
Ms. Ramitha D K

Keywords:

Control Release Fertilizers (CRFs), urea, keratin, nanokeratin, biodegradable polymers

Introduction:

Nitrogen is one of the most important nutrient that has a direct effect on growth, development and yield of crops [1]. The effect of different levels of nitrogen on plant growth and yield has been studied widely. Studies show that increased level of nitrogen results in increased cob number, cob length, cob diameter and grain weight in maize [2], higher value of all the yield contributing characters in groundnut [3], finger millet [4] and in rice [5]. The primary nitrogen source for plants in India is urea as a fertilizer. In the year 2022 - 23, the total consumption of urea was 35.73 million metric tonnes, of which 6.9% was consumed by the state of Karnataka [8]. The disadvantage of using urea fertilizers is that it has a nutrient use efficiency (NUE) of less than 30% [1,6]. The unused fertilizer is lost to the environment by leaching, denitrification, surface runoff and volatilization which is a major concern to the environment [6,7]. Once applied, it releases a large amount of active nutrient species in the early stages of plant growth and leaving very little for later stages. Since plants can absorb only small amounts of the applied fertilizer, it demands multiple addition of the fertilizer [9]. To overcome this, we can employ control release fertilizers (CRFs) which can be formulated to release nutrients timed according to the plant’s needs [7]. Various materials such as sulphur and polyurethane have been used to coat urea to achieve controlled release. However, the problem associated with such coating materials is that they make the soil acidic (as in the case of sulphur coated urea), non – biodegradable (as in the case of polyurethane coated urea) and their nitrogen release profiles are still not satisfactory [18]. Hence, additional research is required to make the CRF completely biocompatible and accurately time the release of fertilizer based according to the plant's need [9].

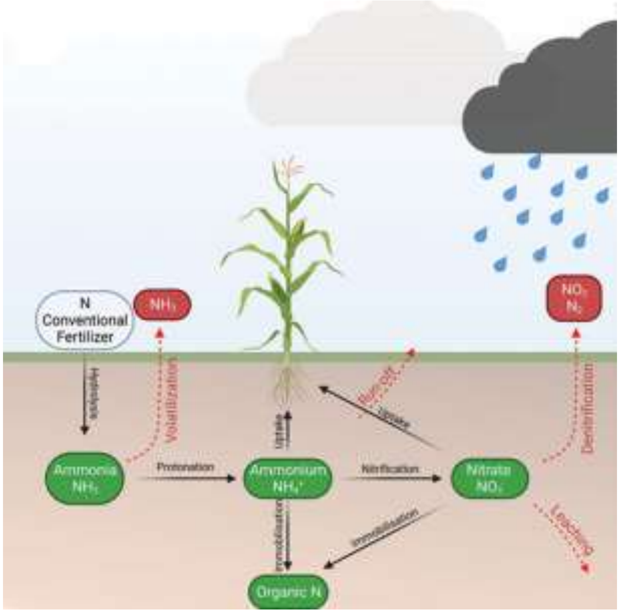


Figure 1: The fate of conventional N fertilizer [9]

Therefore, our work aims to synthesize a composite of nanokeratin - extracted from waste human hair - with urea and coat the resulting material with biodegradable polymers such as polyethylene glycol (PEG) and ethyl cellulose in different formulation to achieve control release of nitrogen. Since urea dissolves quickly, it serves as an immediate nutrient source to the plants [12]. Whereas, keratin degrades slowly and provides nutrients at later stages of plant growth. Moreover, keratin, being a sulphur rich protein, can also serve as a nitrogen and sulfur source to the plants [5,12].

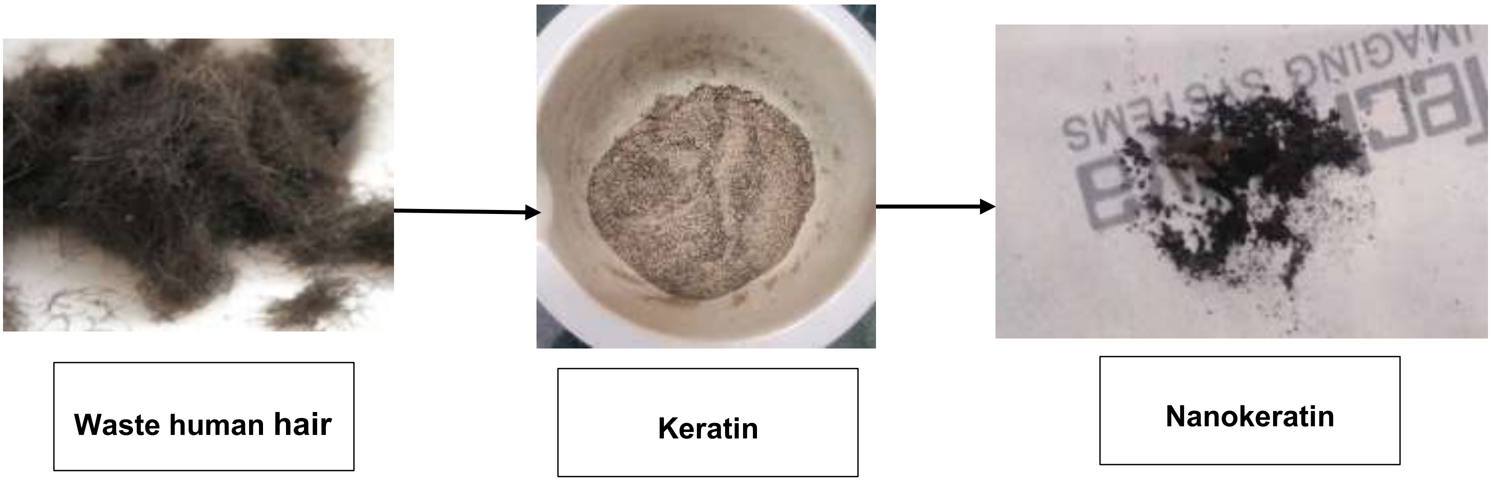
Objectives:

1. Extract nanokeratin from waste human hair that is usually disposed by the local barber shops.
2. Synthesize a composite of urea and nanokeratin.

3. Coat the material with biodegradable polymers like polyethylene glycol (PEG) or ethyl cellulose.
4. To study the surface morphology of the coating by SEM.
5. Study the nitrogen release characteristics of the synthesized CRF in water and confirm if the synthesized CRF meets the criteria for CRF set by European Committee for Standardization (CEN).
6. Compare the synthesized fertilizer with other commercially available CRFs like sulfur coated urea and neem coated urea.

Methodology:

1.Typical Synthesis of nanokeratin: The human hair samples are washed and thrice rinsed thoroughly with distilled water to remove all dirt. After drying, the hair fibres are dissolved in 1M NaOH solution and mixed at 40^0C for a period of 1-2 hours. After 1-2 hours, the mixture is filtered by using Whatman filter paper. The aliquot is centrifuged for 10 minutes at 5000rpm and the supernatant is recovered and the pH of the solution is maintained at 2 - 3.5 to precipitate out the keratin from the hydrolysate, using 1N HCL. The solution is filtered and Keratin is obtained as precipitate and dried at 45^0C for 2 hours [13]. Dissolve the extracted keratin (0.5 g) in 10 ml of deionised water and ultrasonicate it. Then 40 ml of ethanol is added to the mixture under constant stirring, followed by 5 µl of 8% glutaraldehyde as a crosslinker. The mixture is stirred overnight to enable the formation of keratin nanoparticles and is kept undisturbed for 24 h. The precipitate is collected by centrifugation at 20,000 rpm for 20 min and the collected keratin nanoparticles are dried at 50 °C for 24 h [12].



Scheme 1: *Synthesis of nanokeratin from human hair*

Future work:

2.Typical Synthesis of nanokeratin/Urea/PEG or ethyl cellulose CRF: The synthesized keratin nanoparticles (1 g) is dispersed in distilled water (4ml) by ultra-sonication for 45 min. This dispersion is mixed with urea solution (8.5g/5ml) at room temperature for 12 h. As a result, white precipitate is obtained which is allowed to settle and the excess liquid is decanted [12]. Make a suspension of nanokeratin/urea in 30mL chloroform followed by dissolution of 1.75g of PEG or ethyl cellulose under constant stirring at a temperature of 60-90^{0}C. Add 20g of urea granules to the solution under constant stirring for an hour. Evaporate the solvent to obtain the CRF.

3. Study of nitrogen release characteristics of the synthesized CRF in water: The CRF (0.1 g) is placed in a tea bag. Soak the tea bag in 400 mL distilled water. 2 mL of solution is taken out to detect urea release using UV-visible spectrophotometer after every 10 min. 2 mL distilled water to the system is added each time and the sample is taken for measurement to maintain a constant quantity of solvent [14].

Results and Discussion:

From an extensive work for one month, we were able to extract keratin from waste human hair collected from local barber shops and also synthesized nanokeratin. Synthesized keratin and nanokeratin were characterized by X – Ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy.

Characterization:

X – Ray Diffraction:

All the samples were characterized by powder X – Ray diffraction (XRD) using a Philips X'pert Pro diffractometer (Cu Kα radiation, secondary graphite monochromator, 2° 2θ per min) with 2θ range from 5° to 70°.

1. Keratin:

XRD diffractogram shows the characteristic broad peak of keratin at 2θ=20°, indicating that the synthesized keratin particles are semi – crystalline to amorphous in nature [16].

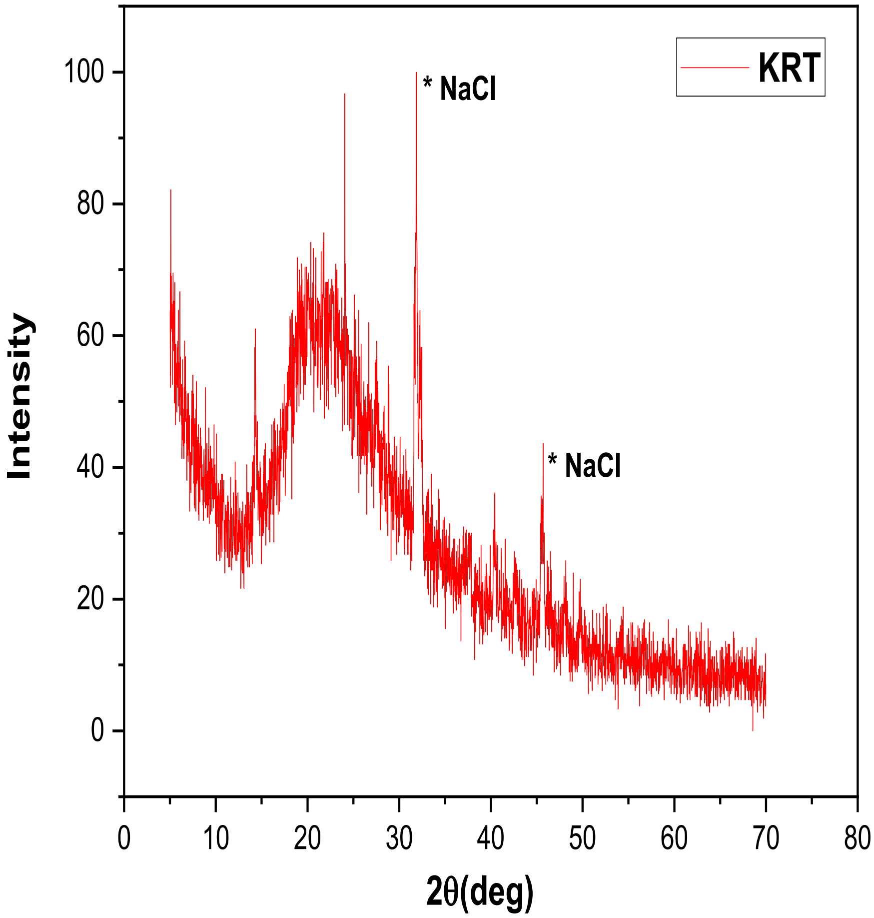


Figure 2: XRD of keratin

2. Nanokeratin:

The **XRD of nanokeratin** matches that of keratin. The peaks are broad and this may indicate that the keratin particles are in the nanoscale. This can be further confirmed by carrying out SEM studies.

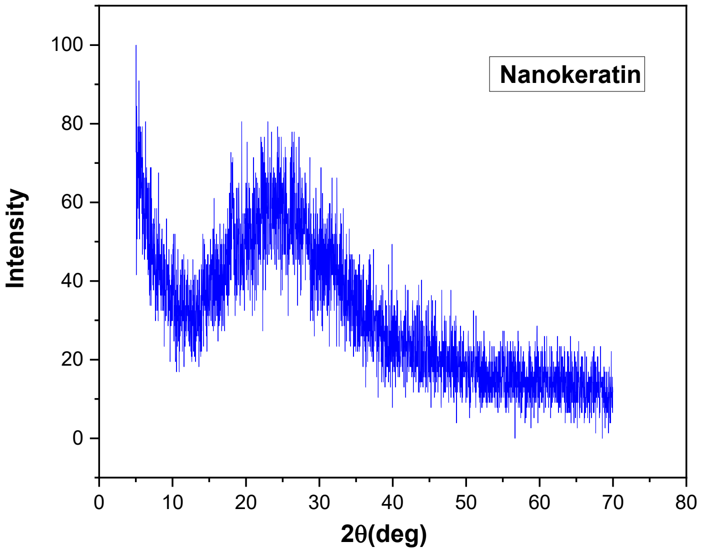


Figure 3: XRD of nanokeratin

Fourier Infrared Spectroscopy:

All the samples were characterized using FTIR spectrometer with ATR (Bruker Alpha 11) in the transmission mode in 4000 cm^{-1} and 600 cm^{-1} wavenumber range.

1. Keratin:

The FT-IR spectrum consists of a band centered around 3323 cm^{-1}, which is due to O-H bond symmetric stretching vibration, 3254 cm^{-1} due to N-H bond asymmetric stretching, 2949 cm^{-1} due to C-H bond symmetric stretching in CH3 terminating groups, 2726 cm^{-1} due to C-H bond symmetric stretching in CH2 groups, 1577 cm^{-1} due to C=O bond symmetric stretching, 1118 cm^{-1} due to C-N bond stretching, and 619 cm^{-1} due to C-S bond symmetric stretching. These bands are characteristic to keratin [16].

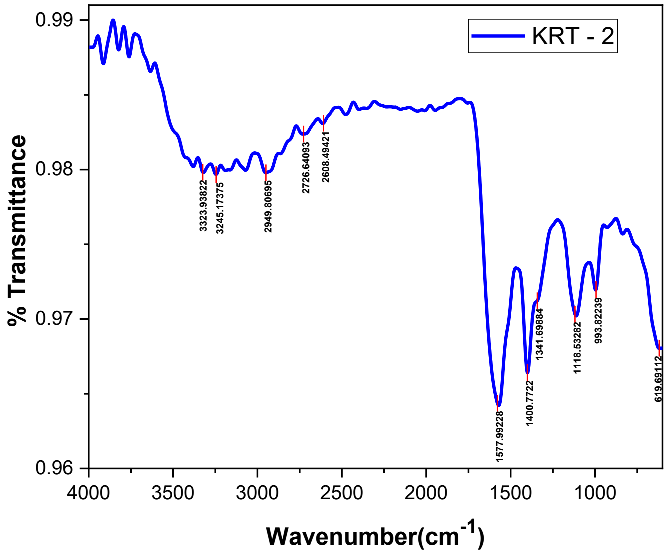


Figure 4: FTIR of keratin

2. Nanokeratin:

The **FTIR spectrum of nanokeratin** contains all the prominent peaks as seen in the case of keratin. The peak at 1322 cm^{-1} represents the aldemine peak, which confirms the crosslinking of keratin peptide chains by glutaraldehyde [17].

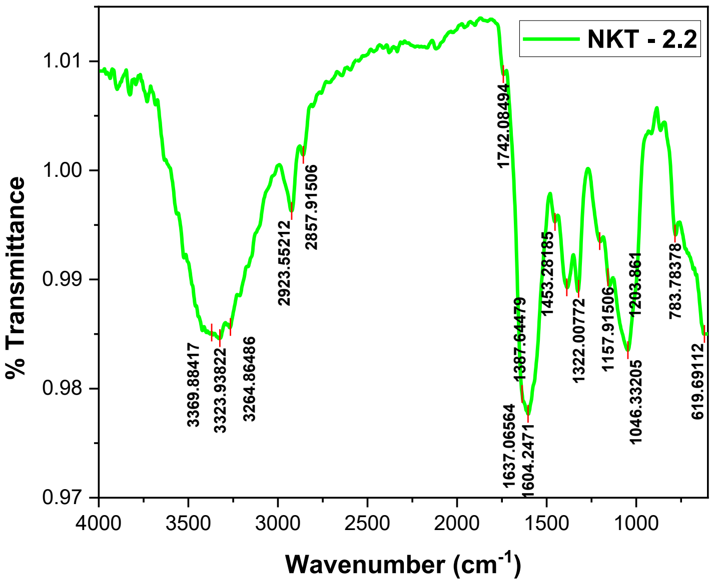


Figure 5: FTIR of nanokeratin

Project Outcome & Industry Relevance:

This project aims to address 2 central environmental issues:

(i) the challenge of disposal of waste human hair into the environment.

(ii) the adverse effects of conventional urea fertilizers on environment.

A whopping sum of 3 – 4 tonnes of waste human hair is disposed annually in our country, which poses a very big environmental problem [15]. Also, as mentioned earlier, in the year 2022 - 23, the total consumption of urea in our country was 35.73 million metric tonnes, of which 6.9% was consumed by the state of Karnataka. Given this scale of waste human hair generation and the use of urea as primary N fertilizer, this work presents a plausible solution that can be explored further and thus is highly relevant in the waste management and fertilizer industries.

Thus, our work aims to convert biowaste into sustainable materials and directly contributes to the Swachch Bharath Mission (SBM) of Government of India.

Working Model vs. Simulation/Study:

This project involves the development of a physical working model.

Project Outcomes and Learnings:

Project outcomes: At the end of one month of work, we were able to synthesize nanokeratin from waste human hair, which will be used to make a composite with urea to make different formulations of CRFs during the remaining leg of our project.

Learnings:

1. Research methodology.
2. Structured and organized approach towards problems and hiccups.
3. Insight into the waste management and fertilizer landscape of our country.
4. We learnt that high yield of keratin can be extracted from waste human hair through dialysis.

Future Scope:

The future scope of this project includes:

1. **Material development and optimization:** to explore other methods of synthesis that could help achieve a good coating on urea. Optimize the thickness of the coating material and the amount of keratin used in order to achieve the best control release of nutrients.
2. **Study on factors affecting control release:** to study the effect of temperature, soil type, pH, and different bacteria present in the soil and other environmental factors such as humidity on the nutrient release profile of the synthesized CRF.
3. **Testing on larger fields:** to test the performance of the synthesized fertilizer on farm fields where there is no control over the surrounding environment.
4. **To study the effect of CRFs on plant growth:** to study the plant growth in terms of morphological and physiological changes when CRFs are administered and compare it with other commercially available CRFs and non-coated fertilizers.
5. **To develop highly specific CRF formulations:** based on the influence of environmental factors on the control release, it would be possible to formulate a CRF that is highly specific to a particular crop and a particular soil type.
6. **Scalability and cost effectiveness:** to develop industrially scalable techniques which are very cost efficient so that CRFs can replace the conventional fertilizers in the market.