

## Original Research Article

# Development of carbon-based N fertilizer for reducing N loss and improving nitrogen availability

### ABSTRACT

Comment [MOU1]: Add background

**Aims:** Synthesis and characterization of carbon-based nitrogen fertilizer and assess the nitrogen releasing pattern of newly synthesized N fertilizer.

**Study design:** The experiment was laid out in Completely Randomized Design (CRD) with seven treatments in three replications.

**Place and duration of study:** The incubation study was conducted in the Soils and Environment post-graduate laboratory at Agriculture College and Research Institute, Tamil Nadu Agricultural University, Madurai-625104, India from February 2022 to April 2022.

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**Methodology:** Seven treatments were tested with various combinations of N fertilizers viz., Absolute control-No nitrogen (C), Soil test crop response-based N as urea (STCR-U), Soil test crop response-based N as ammonium chloride (STCR-AC), Carbon-tailored N fertilizer from urea (100% N) (CNF-U100), Carbon-tailored N fertilizer from urea (75% N) (CNF-U75), Carbon-tailored N fertilizer from ammonium chloride (100% N) (CNF-AC100) and Carbon-tailored N fertilizer from ammonium chloride (75% N) (CNF-AC75). The characterization of carbon-tailored N fertilizers and their impact on soil available N were analyzed.

**Results:** Among the N fertilizers, carbon-tailored N fertilizer from urea 75% N (CNF-U75) demonstrated the sustained release of N ( $104.0 \text{ mg kg}^{-1}$ ), when compared to the STCR N fertilizers.

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**Conclusion:** A novel carbon-based N fertilizer was tailored by intercalating urea and ammonium chloride with carbon material. The N releasing pattern of CNF-U75 implied that carbon-based N fertilizer is a novel product for sustained N release with higher nitrogen utilization efficiency and lower environmental risks. This study result could be used as a beneficial source of information on the current needs and future perspectives of carbon-based N fertilizer (CNF) in precision farming.

*Keywords: Carbon material, N fertilizer, carbon-tailored N fertilizers*

### 1. INTRODUCTION

Comment [MOU3]: Well written (good)

Nitrogen (N) is often the limiting element for crop growth [1]. However, excessive N fertilizer applications can harm the soil and accelerate nitrate leaching, ammonia volatilization, and nitrous oxide emissions, resulting in low nitrogen use efficiency, high economic costs, and environmental pollution [9][30]. Agricultural N loss threatens climate change, human health, the ecosystem, and global sustainability [29]. Inorganic nitrogen (N) fertilizer is a major source of pollution for water and the environment [3].

Many researchers around the world have realized the importance of this issue and studied various agricultural measures, such as fertilizer management practices [4], controlled-release fertilizer [27], satisfactory tillage system [12], controlled drainage technology, water-saving irrigation [13], and soil amendments [18]. Sustainable agriculture requires improving crop nitrogen use efficiency (NUE) without adding additional fertilizer [20].

Only 50-60% of N is taken up by crops from the direct use of conventional N fertilizers [7]. Due to traditional fertilizer's high solubility, poor thermal stability, and low molecular weight, most nutrients are lost by surface run-off, denitrification, leaching, and volatilization, resulting in low fertilizer use efficiency [24]. Precise use of fertilizers with [the](#) sustained release is essential for enhancing fertilizer use efficiency [15].

In the last 10 years, a lot of research has been done on sustained-release fertilizers, because they may improve nutrient retention and fertilizer effectiveness by limiting nutrient solubility and releasing nutrients in a controlled way, even while providing sufficient plant nutrition [5]. The coating of nitrogenous fertilizers will delay the uptake and usage of fertilizer by their targeted plants; as a result, their targeted [plants](#) uptake and usage time are greater than that of typical nitrogenous fertilizers [8].

The price, non-degradability, and non-renewability of coating materials contribute to environmental and economic implications [19]. Studies have concentrated on bio-based coating materials for the controlled release of nitrogen fertilizers to enhance N usage efficiency and decrease environmental impact [21] [6]. [Carbon](#) [The carbon](#) material is prepared using biomass conversion technology in a reduced oxygen environment [11]. Carbon material may boost nutrient retention, water retention and soil fertility, thereby promoting plant growth and agricultural yield [28] [26].

According to [23], [the](#) carbon material is being used in fertilizer to prevent nutrient leaching and enhance nutrient use efficiency. [2] revealed that a novel idea to improve the sustained release nature of fertilizers is to use a carbon material that has been doped with nutrients. Carbon material, an eco-friendly soil amendment, has dual features of agricultural market importance and ecological benefits due to its effects on enhancing soil characteristics [22] [14], nutrient absorption and crop productivity, reducing N loss in cropland and greenhouse gases.

To produce more eco-friendly slow-release fertilizers, organic acids are being used. Surface functional groups in the carbon material may react with an organic acid and improve the coating resistance. Studies on carbon-based N fertilizers and their interacting effects on soil nutrient content and nitrogen utilization efficiency are scarce in India.

In this context, we compared carbon-tailored N fertilizer with conventional N fertilizer on nutrient release. In this study, we synthesized and characterized the physicochemical and morphological properties of carbon-tailored nitrogen fertilizer (CNF). To assess the impacts of CNFs on soil nitrogen, an incubation study was conducted to evaluate the nitrogen release pattern of CNFs.

## 2. MATERIALS AND METHODS

### 2.1. Study area

The influence of CNFs on soil nitrogen availability was evaluated using an incubation experiment. The incubation study was conducted in the Soils and Environment post-graduate laboratory at Agriculture College and Research Institute, Tamil Nadu Agricultural University, Madurai-625104, India. Materials and experimental techniques adopted for conducting experiments were described in detail.

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### 2.2. Carbon material production and neutralization

*Prosopis juliflora* wood was used to make carbon material. A woodcutter was used to cut the raw material into 10-15cm long pieces. To remove moisture, the cut wood was sun-dried for 10 days. It was then heated to 450°C in a pilot-scale slow pyrolysis system designed by the Department of Soils and Environment and funded by DST SERB. Temperature sensors and an electronic control system for N<sub>2</sub> gas flow and oil collection are included in the device [16].

A stainless-steel lid was used to encapsulate the five kg of raw material. The pyrolysis temperature was set at 450°C and the residence period was set to 6 hours. To maintain an inert environment during pyrolysis, nitrogen gas was supplied at a constant pressure. After 6 hours, the unit was left to cool for two hours, and fresh carbon material was collected and stored in another container for future processing. Then, the collected fresh carbon material was crushed and sieved to match the particle size of the soil.

The pH of the prepared carbon material is alkaline (9.85). A direct blending of nitrogen fertilizer with raw carbon material will cause the ammonia in the fertilizer to volatilize. Raw carbon material was neutralized with acetic acid before nitrogen intercalation. Initially, we created 1, 2.5, and 5% acetic acid by dissolving 10, 25, and 50 mL of acetic acid in distilled water and diluting it to 1000 mL. The produced acetic acid was gently poured into the new carbon material in a 0.5:1 ratio (500 mL of acetic acid in 1000 g of carbon material) and well stirred. The pH was evaluated after a week, and 5 percent acetic acid resulted in a significant fall in raw carbon material pH to 7.2. Following positive results, the whole amount of carbon

material required for the study (3.5 kg) was neutralized with 5% acetic acid. The characteristics of raw carbon material was depicted below (Table 1).

**Table 1. Characteristics of carbon material**

S. No.	characters	<i>Prosopis</i> carbon material
1.	Moisture (%)	1.49
2.	Ash (w w <sup>-1</sup> )	1.41
3.	Bulk density (g cm <sup>-3</sup> )	0.51
4.	Particle density (g cm <sup>-3</sup> )	0.68
5.	Pore space (%)	64
6.	pH (1:10 solid water suspension)	9.85
7.	EC (dS m <sup>-1</sup> ) (1:10 solid water extract)	0.24
8.	Cation exchange capacity (c mol (p <sup>+</sup> ) kg <sup>-1</sup> )	18.7
9.	Total carbon (g kg <sup>-1</sup> )	529.60
10.	Total Nitrogen (g kg <sup>-1</sup> )	3.2
11.	Total Phosphorous (g kg <sup>-1</sup> )	1.04
12.	Total Potassium (g kg <sup>-1</sup> )	3.1
13.	Calcium (g kg <sup>-1</sup> )	12.5
14.	Magnesium (g kg <sup>-1</sup> )	0.43

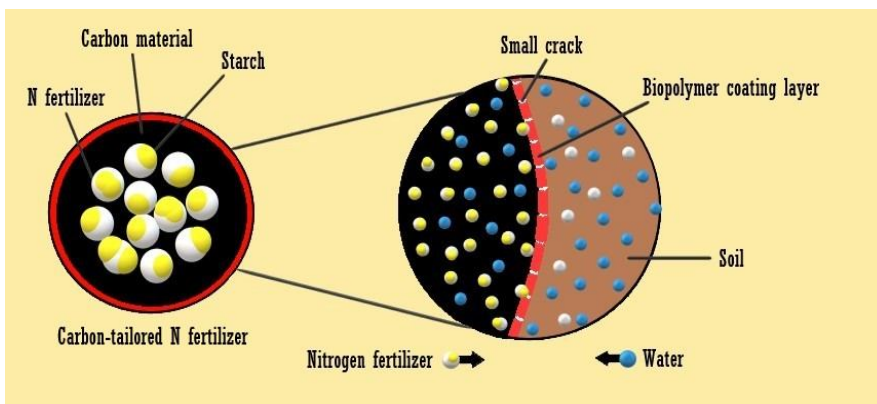
### 2.3. Preparation of carbon-tailored N fertilizer and characterization using XRD and XPS analysis

CNF was prepared using urea and ammonium chloride as nitrogen sources. Depending on the surface area, high porosity, and fertilizer quantity, the carbon material, and fertilizer mixing ratio was established at 1:2. Before the commencement of the experiment, initial soil was gathered from the experimental area and tested for pH, EC, organic carbon, and accessible N, P, and K. The crop N demand was calculated using the standard Soil Test Crop Response (STCR) equation. Based on the N content, the fertilizer N needed was estimated and converted to urea and ammonium chloride.

For the experimental soil, the STCR recommendations were 193.9 kg of N, 11.21 kg of P<sub>2</sub>O<sub>5</sub>, and 146.76 kg of K<sub>2</sub>O. The amount of carbon material needed was calculated based on the quantity of urea and ammonium chloride necessary for the research. Starch was combined with N fertilizer before being added to carbon material as a binding agent. To control N release, carbon-tailored N fertilizer was covered with organic acid (biopolymer). Because of its porous structure, carbon material holds N fertilizer and slowly

releases it when exposed to water. Using the preceding method, we developed a new carbon-based N fertilizer. Below is a step-by-step tutorial and pictorial illustration for producing CNF (Figure 1).

- Nitrogen fertilizer  
(STCR basis)
- Starch as a sticking agent  
(20 g of starch to 1 kg of N fertilizer)
- Mixing with neutralized carbon material (pH 7.2)  
(500 g of carbon material to 1000 g of N fertilizer)
- Layering with organic acid as a biopolymer coating  
(50 mL of humic acid to 1000 g of carbon material mixed fertilizer)
- Carbon-tailored N fertilizer  
(Final product)



**Figure 1. Schematic diagram of controllable N releasing mechanism of a CNF**

The surface composition and crystalline structure of raw carbon material, CNF from urea, and ammonium chloride were analyzed using X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD), respectively.

#### **2.4. Incubation experiment**

Soil samples were collected from the experimental site, sieved using a 2 mm sieve, and used to conduct an incubation experiment. The experiment was conducted in a completely randomized design (CRD) with three replications. To evaluate the nitrogen releasing pattern of newly designed CNFs, 500 g of soil was placed in each plastic pot and nitrogen sources were added based on the STCR approach in the form of

urea, ammonium chloride, carbon-tailored urea and ammonium chloride. The experimental setup was incubated for 10 weeks at field capacity moisture level. Treatment C was kept as an absolute control (no nitrogen). Soil samples (30 g) were collected at weekly intervals and shade dried. The standard methodology for soil N analysis was ~~adapted~~ adopted.

## 2.5. Data treatment and statistical analysis

The measured data was represented by ~~the mean and standard deviations of three replicated samples~~ three replicated samples' mean and standard deviations. All of the data was processed using Excel 2019. For statistical analysis, the program SPSS 22.0 was used. The treatment differences were evaluated using one-way ANOVA, with significance set at  $p < 0.05$ .

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of CNF using XRD and XPS

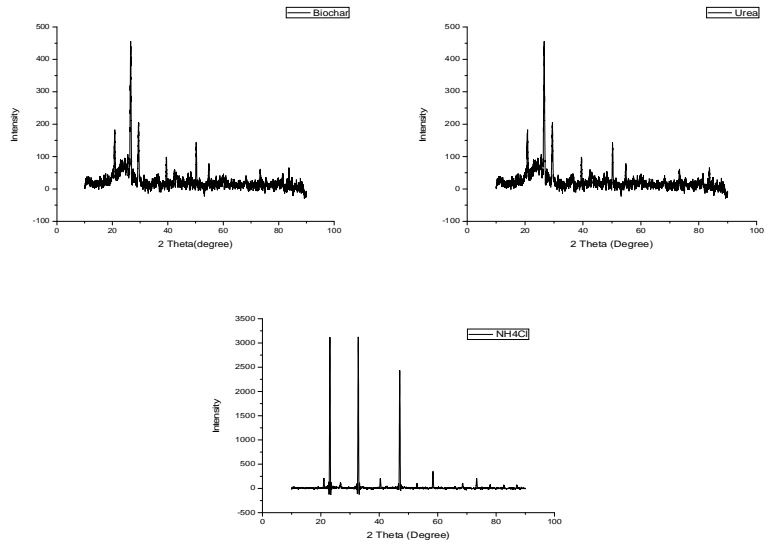
X-ray Diffraction patterns of raw carbon material, CNF from urea, and ammonium chloride were depicted in Figure (2. a, b and c). The findings showed that when urea and ammonium chloride were loaded onto the extremely disordered carbon material, its structural integrity altered to crystalline peaks. The  $2\theta$  data of 21, 28, 30, 40, and 50 peaks verified N loading on the carbon material.

The typical diffraction was observed in the XRD patterns of raw carbon material, CNF from urea and ammonium chloride at  $2\theta = 21^\circ, 28^\circ, 30^\circ, 34^\circ, 40^\circ, 48^\circ, \text{ and } 50^\circ$ , showing that carbon material was efficiently filled and loaded with urea and ammonium chloride. The substrate's state had shifted from amorphous to crystalline, as verified by XRD [18].

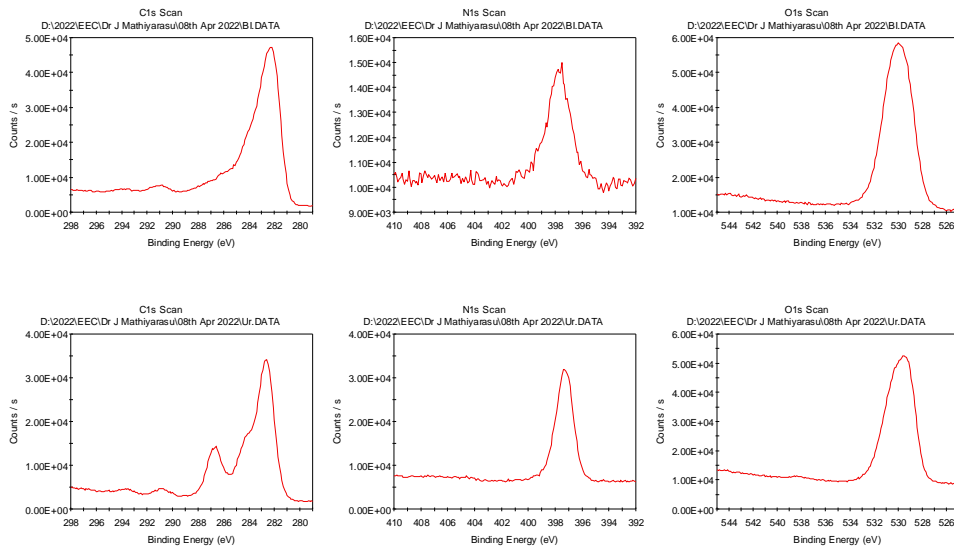
The surface elemental composition and chemical bonding of the CNF from urea and ammonium chloride were characterized using XPS, and the findings were compared to that of raw carbon material. The XPS assay confirmed that carbon material and CNF from urea and ammonium chloride were mostly constituted of C, N, and O which corresponded with the elemental analysis findings.

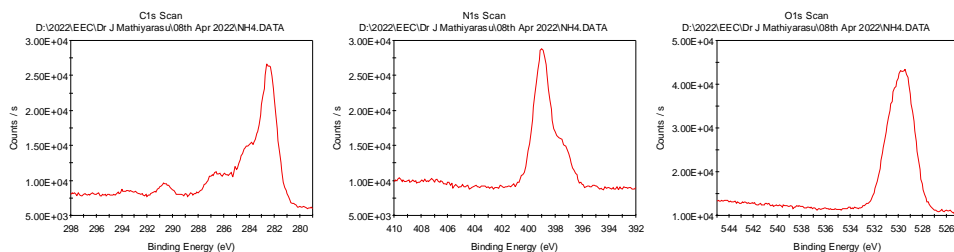
The C1s spectra (Figure 3. a, d and g) showed three peaks at 279, 283.1, and 298 eV (carbon material), 279, 283.64, and 298 eV (CNF from urea), and 279, 283.32, and 298 eV (CNF from ammonium chloride), which were ascribed to C-C, C=C, and COOR (R=H, N), respectively. The N1s peaks (Figure 3. b, e and h) at 392, 397.79, and 410 eV (carbon material), 392, 397.35, and 404.72 eV (CNF from urea), and 392, 398.83, and 405.96 eV (CNF from ammonium chloride) represent nitrogen in the form of N-C, N-H, and amine III C-NH ((C)<sub>3</sub>-N) groups. Peaks in the O1s spectra (Figure 3. c, f and i) indicate the presence of bentonite at 525, 530.16, and 545 eV (carbon material), 525, 530, and 545 eV (CNF from urea), and 525, 530.06, and 545 eV (CNF from ammonium chloride), related to C-OH, COOR (esters, anhydrides), and C=O groups. Similar results for XRD and XPS were also found by [18].

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**Figure 2. X-ray diffraction pattern of carbon material (a), CNF from urea (b) and CNF from ammonium chloride (c)**





**Figure 3. X-ray photoelectron spectroscopy of carbon material - C1s (a), N1s (b) and O1s (c), CNF from urea - C1s (d), N1s (e) and O1s (f), and CNF from ammonium chloride - C1s (g), N1s (h) and O1s (i)**

### 3.2. Evaluation of CNF on nitrogen releasing pattern using incubation experiment

An incubation experiment was conducted to assess the ~~nitrogen-releasing~~ nitrogen-releasing pattern of CNFs. According to [17], ~~the~~ Sustained release of fertilizer formed from carbon material may delay the nutrient release, enhance soil permeability, lower soil bulk density, and store carbon in the soil. The treatment CNF-U75 achieved a sustained release of 104.0 mg kg<sup>-1</sup> of soil available N, which is comparable with CNF-AC75 (104.2 mg kg<sup>-1</sup>), followed by CNF-U100 (106.4 mg kg<sup>-1</sup>), which was on par with CNF-AC100 (106.7 mg kg<sup>-1</sup>) in the first week of the trial and gradually increased over the next few weeks when compared to the STCR N fertilizers (Figure 4). The least soil available N was recorded in absolute control (no nitrogen).

The nutrient release rate of carbon-tailored N fertilizer was influenced by the composition of the coating material (organic acid). When compared to STCR urea and ammonium chloride, carbon-tailored N fertilizers generated a greater result in terms of sustained release pattern of nitrogen over 10 weeks. This is due to the sustained release characteristic of carbon material and the biopolymer coating (organic acid) on N fertilizers. Because of its high aromatic stability and porous structure, carbon material can be used as a coating material for ~~the~~ sustained release of nutrients [10].

When compared to chemical urea, the carbon-tailored urea composite was proven to be capable of delayed N release and keeping a high proportion of ammonium to nitrate over a longer period [25]. Based on these data, it was concluded that carbon material and organic acid are critical elements in reducing N loss. When compared to STCR-U and STCR-AC, carbon material stores nitrogen in its large surface area and pore volume, resulting in gradual nitrogen release and reduced nitrogen losses regardless of soil depth.

Furthermore, organic acid coating lowers solubility, resulting in prolonged nitrogen release and hence decreasing nitrogen loss under CNF. The high porous structure and nutrient-holding ability of carbon material facilitated the slow release of N fertilizers into the soil profile at the proper period. Based on the findings, it was inferred that CNFs release nitrogen slowly and reduce N loss compared to conventional fertilizers. The graph (Figure 4) below shows the result of the incubation experiment.

**Figure 4. Nitrogen releasing pattern of carbon-tailored N fertilizer using incubation experiment**

#### **4. Conclusion**

In this study, a sustained release N fertilizer was prepared by intercalating nitrogen fertilizer into a carbon material at the ratio of 2:1. Among the fertilizers, CNF-U75 resulted in sustained N release compared to conventional N fertilizers. We conclude that the carbon-tailored N fertilizer is a novel option for the synthesis of controlled releasing N fertilizers, which may pave way for creation of a new generation of sustained release fertilizers. Sustained release N fertilizer made on carbon material is a potential product for soil health sustainability, as well as a clean technology for minimizing N loss and enhancing crop production in susceptible regions.

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