

# Urea Intercalated Biochar—a Slow Release Fertilizer Production and Characterisation

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## Abstract

A laboratory study was undertaken to determine the N release pattern of Urea Intercalated Biochar derived from *Prosopis juliflora*. Biochar was produced by pyrolysing the wood cuttings excluding the bark at 350°C. The resultant biochar was characterized using XRD, FT-IR, Raman Spectroscopy and SEM. After characterization, different forms of nitrogen viz.,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{NH}_2$ , Combined  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were loaded at varying concentrations (20–200 mM) and sorption and desorption characteristics were examined. Among the forms tested, urea fortified with biochar showed lower desorption at levels of N loading concentration. A new biochar based formulation was evolved by intercalating biochar with urea at 1:1 ratio through hydrothermal method. The intercalated urea: biochar (1:1 ratio) fertilizer was characterised using the set of equipments and the total nitrogen was quantified as 30% as per the EDAX values which closely coincided with analytical values. The retention and release pattern of urea intercalated biochar depicts that the biochar derived PJ is a potential substrate that can be exploited to develop slow release N fertilizer with higher use efficiency and less environmental hazard.

**Keywords:** Biochar, Pyrolysis, Slow Release Fertilizer, Sorption, Urea.

## 1. Introduction

Nitrogen continues to be the “kingpin” of nutrient kingdom in agroecosystems. Despite several decades of research, it is hardly possible to enhance the use efficiency with fewer percentages from 30% to 35% through coating of widely used nitrogenous fertilizer (urea) with neem, tar, starch etc [1]. In addition to the organic substances, inorganic substrates such as zeolite, montmorillonite and halloysite minerals have also been introduced to regulate the release of N from conventional urea. These minerals are quite useful but their extraction and purification is time consuming and a costly affair [2]. This necessitated searching for an alternate substrate to regulate the release of N from urea.

Biochar is produced by burning the biomaterials (crop residues and wood wastes) under oxygen limited conditions (pyrolysis) at 350°C for 30 minutes and cooling of the substance overnight. Biochar is used as a soil amendment/conditioner to improve physical phenomena [3]. Among the biomaterials, *Prosopis juliflora* (PJ) wood is known to produce 30% output [4] besides its use as a fuel wood, fodder, charcoal and timber. The carbon content of PJ Biochar is 50–70% [5]. Biochar is microporous in nature, besides extensive surface area ( $120 \text{ m}^2\text{g}^{-1}$ ) that can be exploited for loading of nutrients [6, 7, 8, 4]. This study hypothesized that the biochar can be used as a substrate to regulate the adsorption and desorption of pattern of different forms of N ( $\text{NH}_2$ -N,  $\text{NH}_4^+$ -N,  $\text{NO}_3^-$ -N, combined  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ -N that

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can serve as a base to develop biochar based slow release fertilizers.

## 2. Materials and Methods

### 2.1 Biochar Production

PJ wood samples were collected at Krishnampathi Lake, Coimbatore (11.0183° N, 76.9725° E). The wood (25 cm) without bark was dried at 80°C for 48 hours to remove the moisture and exudates. Washed with deionised water 5 times, the chopped woods (4–5 cm) were dried at 80°C for 48 hours and soaked further in dilute Sulphuric Acid ( $H_2SO_4$ ) to destroy insects and microorganisms. Thereafter, it was dried and slow pyrolysis was followed at temperature of 350°C for 30 mins with resident time of 8 hours. Solid char was rinsed with distilled water 3 times to remove the ash materials and dried. The char was ground in a flour mill and sieved through 0.5 mm. The resultant powder was subjected to physiochemical and structural analysis using standard procedure [9].

### 2.2 Nutrient Loading and Sorption Studies

A gram of biochar was weighed in a centrifuge tube and nitrogen in different forms viz.,  $NH_4^+$ ,  $NO_3^-$ ,  $NH_2$ , Combined  $NH_4^+$  and  $NO_3^-$  were loaded at various concentrations of N from 20 to 200 mM as indicated in the protocol [10]. The polypropylene tubes were laid horizontally in a mechanical shaker and agitated continuously for 24 h followed by centrifugation at 5000 rpm for 10 min. The supernatant was decanted and  $NH_2-N$  and  $NO_3^-N$  was determined spectrophotometrically using Nessler's Reagent and  $NH_4^+N$  was estimated by distillation as suggested in the protocol [11]. The statistical analysis was determined using standard procedures [12].

### 2.3 Intercalation of Urea, Biochar and Characterisation

Urea solution was prepared by mixing by adding deionised  $H_2O$  at 1:1 w/v (10g:10 mL) ratio and the slurry was heated on a hot plate at 105°C with constant stirring till the crystals turned into solution. About 10 g of biochar was mixed thoroughly with the urea solution. The mixture was dried in a hot air oven at 65°C till the moisture is completely exhausted. One gram of adhesive polymer (starch) was added to the mixture and air dried, powdered and used as an urea

intercalated biochar fertilizer. The resultant fertilizer product was characterized using Fourier Transform Infrared Spectroscopy (FTIR) in the range of 600 to 4000  $cm^{-1}$  using Attenuated Total Reflectance (ATR) technique. The FT-IR spectra were detected in a pellet that was prepared by mixing the fertilizer with KBr at the rate of 0.1%.

In order to confirm the loading of N, the Raman Shift was determined using Raman Spectroscopy (Model R 3000 QE). About 1–2 grams of intercalated urea-biochar fertilizer was kept in a glass cuvette and the Raman shift was determined at 785 nm [13]. The fertilizer material was sputter coated with gold before imaging under Scanning Electron Microscope (FEI Quanta 200). About 40–50  $\mu g$  of fertilizer sample was dusted on the carbon conducting tape. In the sample, Energy Dispersive X ray Spectroscopy (EDS) was done to ascertain the elemental composition. The powder XRD patterns of the biochar and urea impregnated biochar (1:1) were recorded using Bruker D8 Advance Powder X ray Diffractometer, Germany.

## 3. Results

### 3.1 Physio-chemical Properties

The PJ biochar had 86.5% C, 1.56% N, CN ratio 55:1, pH 9.16 and EC 0.15  $dSm^{-1}$ . The bulk density, particle density and percent pore space registered in the biochar were 0.50 and 0.71  $g\ cc^{-1}$  and 30%, respectively.

### 3.2 Nitrogen Loading and Sorption

The  $NH_4^+N$  and  $NO_3^-N$  contents of biochar loaded with four forms of N viz.,  $NH_4^+$ ,  $NO_3^-$ ,  $NH_2$  and Combined  $NH_4^+$  at various concentrations (20–200 mM) were quantified at the equilibrium. The desorbed  $NH_4^+N$  in the solution derived from all the four forms N showed a linear pattern correspondingly with the concentrations. Among the forms, urea fortified biochar had the lowest desorption values at all the concentrations. In contrast, biochar loaded with ammonium nitrate had the highest  $NH_4^+N$  regardless of concentrations in Figure 1. Biochar fortified with either  $NO_3^-N$  or  $NH_4^+N$  singly had the similar pattern of desorption in Figure 2.

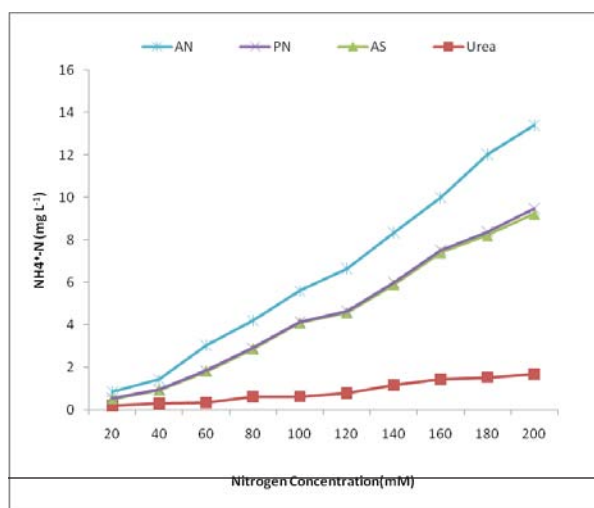
The desorbed  $NO_3^-N$  in the solution derived from various forms N increased with increasing concentrations. Among the forms, urea fortified biochar had the lowest desorption values at all the concentrations. On the

other hand, biochar loaded with ammonium nitrate had the highest  $\text{NO}_3^-$ -N regardless of concentrations. Biochar fortified with either  $\text{NO}_3^-$ -N or  $\text{NH}_4^+$ -N singly had the similar pattern of desorption.

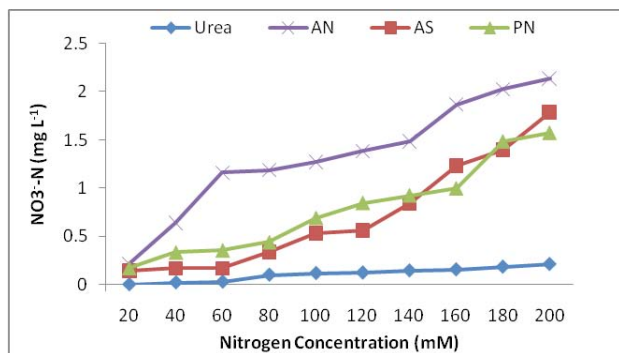
### 3.3 Characterisation

Among the forms of N, biochar fortified urea appeared to retain both nitrate and ammonical N irrespective of various concentrations. Therefore, the characterization was focused only on biochar fortified urea.

The FTIR spectra of PJ biochar and urea impregnated biochar (1:1) fertilizer is shown in Figure 3. The FTIR pattern clearly indicated that the biochar fortified urea had  $\text{NH}_4^+$  peaks of wave number at 2086 to 2804  $\text{cm}^{-1}$  that confirms urea hydrolysis and the resultant  $\text{NH}_4^+$  being adsorbed on the biochar substrate. The Raman shifts of



**Figure 1.** Desorption of  $\text{NH}_4^+$ -N of different forms of fertilizer source on biochar.



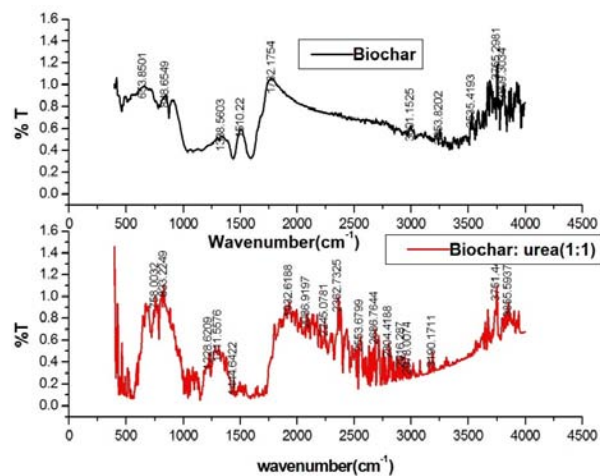
**Figure 2.** Desorption of  $\text{NO}_3^-$ -N of different forms of fertilizer source on biochar.

biochar and urea impregnated biochar (1:1) are shown in Figure 4. The data clearly indicated the adsorption of N that closely coincided at the peaks 1356, 1690 and 1922  $\text{cm}^{-1}$  and confirmed the loading.

The powder X ray Diffraction patterns of PJ biochar and urea impregnated biochar (1:1) fertilizer are depicted in Figure 5. The data revealed that the highly disordered amorphous PJ biochar has changed its structural integrity to crystalline peaks after loading of urea on to biochar. The  $2\theta$  values of 22, 25, 29, 32, 36, 41, 45 and 49 peaks confirmed N loading on to the biochar.

The Scanning Electron Micrographs (SEM) with EDS of PJ biochar and urea loaded biochar are shown (Figures 6 & 7). It showed the disordered carbon and porosity of slow pyrolysed PJ biochar particles. Micropores increased with the combined effect of water and temperature. The pores are scattered in nature and presence on all surface with wide range of size (1.5 to 8  $\mu\text{m}$ ) and shape. Micropores used to improve water and nutrient holding capacity.

Pyrolysed biochar at low temperature might be a suitable adsorbent for controlled/slow release of fertilizer nutrients and which contains carbon and oxygen of more than 98 per cent. After impregnation of urea on biochar, the nitrogen adsorbed on micropores was confirmed through EDS. ~30% of nitrogen present on all places of microporous surface of biochar and internal surface pores were utilised for loading of N by slow diffusion. As a coating agent, sucrose (10%) solution were used to keep intact of nitrogen on biochar internal surfaces.



**Figure 3.** FTIR spectra of biochar and urea loaded biochar (1:1).

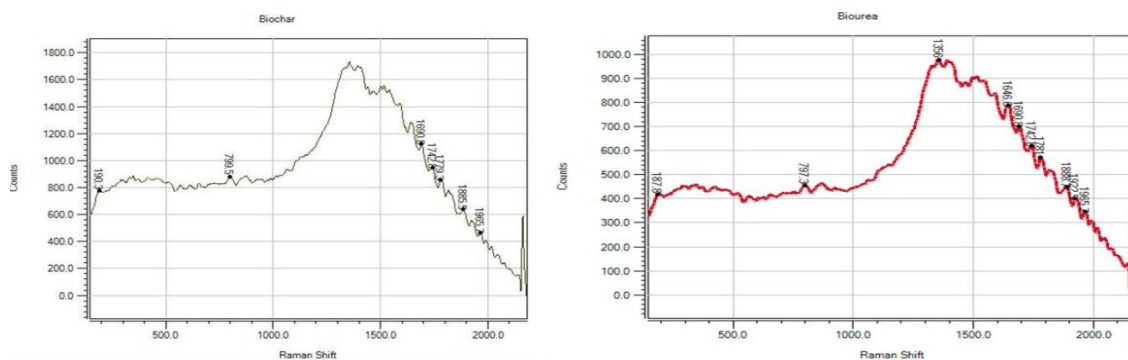


Figure 4. Raman shifts of biochar and urea loaded biochar (1:1).

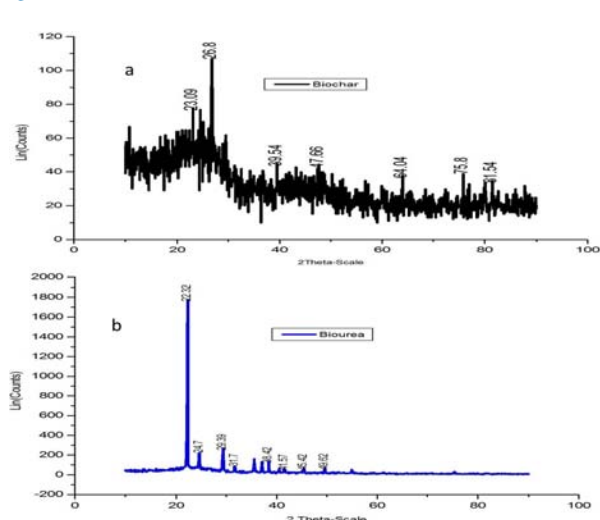


Figure 5. Powder X ray diffraction patterns of a) biochar and b) urea loaded biochar.

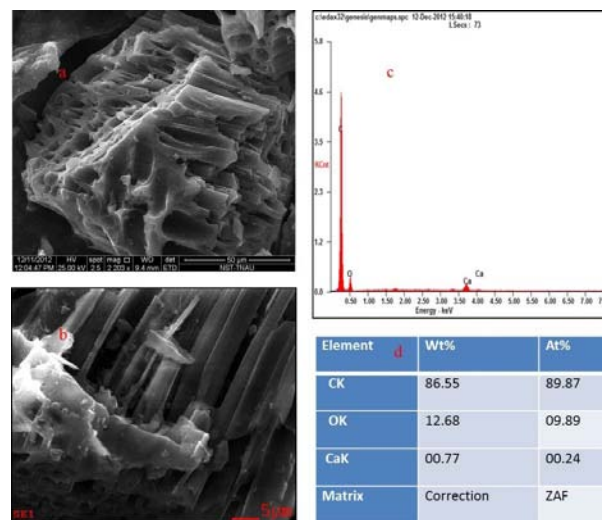


Figure 6. a). Scanning micrograms of PJ biochar b-d). Quantitative composition biochar with EDS.

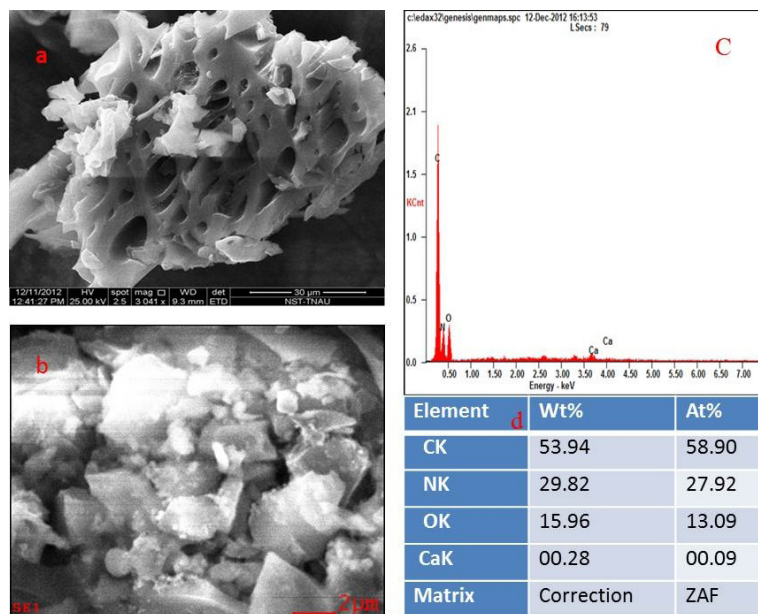


Figure 7. a) Urea impregnated biochar. b-d) confirmation of N loaded on biochar with EDS.



## 4. Discussion

Biochar is gaining popularity to use as a substrate to adsorb or desorb nutrients in order to evolve slow release or controlled release of fertilizers by exploiting its extensive surface area. The quality of biochar varied with tree species and PJ has been evaluated as the best and widely used for soil amendments [14]. Adsorption of ammonium ion by coconut shell activated carbon from aqueous solution was reported [15] previously. Initially, the biochar was characterised through EDAX and recorded the highest carbon content of 86% with C:N ratio of 55 and the data closely coincided with earlier reports [14].

Desorption pattern of N clearly indicated that the biochar fortified with urea had the least and the biochar based urea intercalated had the highest. The data are in conformity with the observations made [16] previously, where it was shown similar desorption pattern for ammonium. It is obvious that least amount of desorption indirectly indicates the retention of N in the biochar intercalated urea while reverse is true with  $\text{NH}_4^+$ -N. The data support that the biochar-urea is a potential source of slow release fertilizer that is very pertinent to promote N use efficiency while minimizing the environmental hazard [17].

Since the urea intercalated biochar area had the lowest desorption, this form was studied further for its properties. The biochar intercalated with urea was characterized using FT-IR, Raman Spectroscopy, XRD and besides SEM imaging. The FT-IR results have shown the  $\text{NH}_4^+$  peaks that may be due to the urea hydrolysis and adsorption of resulted  $\text{NH}_4^+$ . The findings closely corroborate with other reports wherein the loading of  $\text{NH}_4^+$  was detected with the same set of peaks appeared in the same wavelengths [18]. Further, the XRD pattern suggests that the loading of  $\text{NH}_4^+$  shrinks the  $2\theta$  of biochar intercalated urea from 23 to 22. This process had changed the state of the substrate from amorphous to crystalline confirmed both by XRD and SEM imaging [19–22].

## 5. Conclusions

This research findings depicts that the biochar derived PJ is a potential substrate that can be exploited to develop slow release N fertilizer with higher use efficiency and less environmental hazard.

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