Impact of Urea-Intercalated-Biochar on N-Release in Soil and Humified Soil Organic Matter

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Abstract

This research investigated the impact of urea-intercalated-biochar (ICB) on nitrogen release as well as on humified soil organic matter (SOM) distribution in highly weathered soil. Incubation studies were performed with a typical dystrophic red Ultisol and with 10 treatments: soil without amendment (control, CON), soil with three doses of biochar (BC75, BC145, and BC 290), and soil with ICB doses (ICB75, ICB145 and ICB 290). BC and ICB were characterized by ¹³C Nuclear Magnetic Resonance ¹³C-NMR CP/MAS spectroscopy and elemental analyses. Nextractable forms were periodically determined by Kjeldahl method and humic substances (HS) distribution was analyzed on the 28th day after incubation begins (DAI). Intercalation of urea in BC increased sample N content from 2.7 to 22 %, whereas that of C decreased from 40 % to 28 %. As a consequence, C: N decreased from 14.9 to 1.3. The ^{13C} NMR spectra of BC and ICB were similar but relative abundance of major organic functional groups differs, for example, ICB presented a greater proportion of C=O groups due to the carbonyl group of urea and a greater proportion of N/O alkyl C, O-alkyl C, and anomeric C groups due to the addition of starch. There was a significant increase in the concentration of extractable N-NH₄⁺ by addition of urea from the onset of incubation down late period and a significant difference (P > 0.05) was obtained between the ICB and BC over time. This could be as a result of the less accessible form of N in the biochar materials due to the pyrolysis process. There was no evidence of extractable N-NO₃⁻ ion until 14 DAI, significant difference in N-NH₄⁺ concentrations at 28 DAI between the ICB and control was observed over time and the highest value recorded from ICB treated pots at 145 and 290 kg N ha⁻¹.

Keywords: slow-release, humic substances, chemical composition, C sequestration, biochar

1. Introduction

Nitrogen (N) is one of the essential nutrients required by plants in the largest quantity and, most frequently the limiting factor in profitable crop production (Obigbesan, 1999; Mikkelson and Hartz, 2008; Fabiano 2011; Walworth, 2013; Adepetu *et al.*, 2014; Muhammad *et al.*, 2020). Studies have shown that a large portion of the nitrogen applied as fertilizer is not used by plants but lost via runoff, gaseous emissions, erosion and leaching thereby creating economic and serious environmental problems (Bhattacharje *et al.*, 2008; Fageria, 2008; Manikandan and Subramanian, 2015 Bijay-Singh and Eric Craswell, 2021). Urea, Ammonium sulphate and Ammonium nitrate are some of the commonly used N fertilizers in Nigeria with Urea containing the largest percent N (Adepetu *et al.*, 2014). Nitrogen (N) in the form of nitrate is very soluble and mobile thus causing pollution of both surface and ground waters, the problem is aggravated through continual application of Urea fertilizer which has contributed to its low N use efficiency (Muhammad et al., 2020; Bijay-Singh and Eric Craswell, 2021).

The widespread of ground water pollution has been attributed to increase in the quantity of urea fertilizer applied as a result of intensive agriculture (Glibert et al., 2006; Bhatnagar and Sillanpaa (2010) Bijay-Singh and Eric Craswell (2021). Globally, plants N use efficiency is one of the major challenges facing farmers and over the years,

different methods have been employed to improve N Use efficiency with some level of impact on crop production yet to be realized hence, there is the need for a better nitrogen utilization efficiency (Rütting *et al.*, 2018). Biochar has been observed to have chelating abilities and therefore urea being used by farmers need another source that can be used in combination with it in order to slow down the release of N, thereby leading to high N-Use efficiency, increase in N content of the soil, improvement in the soil structure and reduction of soil acidification. Our hypothesis is that intercalating urea with biochar will slow down the release of N.

The study aimed at assessing the N release as well as the ability of the chelated compound to affect the production of humified organic matter and the distribution of the humic substance fractions, thereby providing additional information on its effectiveness in improving nutrient holding capacity of the soil.

2. Material and Methods

2.1 Preparation of Urea Intercalated Biochar (ICB) and Characterization

The Biochar (BC) employed for the synthesis of ICB was produced at 400°C from the aerial part (leaves and branches except roots) of water hyacinth (Eichornia crassipes) at the Federal University of Sergipe - Aracaju / Brazil, in a previous study (Botezzini, 2019, n.p.). Biochar was previously ground in an agate gral. Urea solution was prepared from a commercial sample by adding deionized H₂O 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. 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 was completely exhausted. One gram of adhesive polymer (starch) was added to the mixture and air dried inside the desiccator for 3 days (Manikandan and Subramanian, 2013 18), thereafter, ICB was powdered.

2.2 Characterization of BC and ICB Samples

Nuclear Magnetic Resonance (¹³C-NMR CP/MAS) spectroscopy and Fourier Transform Infrared Spectroscopy (FTIR) were used to determine the chemical compositions of BC and IBC. The nuclear magnetic resonance spectroscopy used was an Agilent Technologies, model DD2, 500 MHz, using zirconium rotors of 4 mm OD with KEL-F-caps. The cross polarization magic angle spinning (CP/MAS) technique was applied during magic-angle spinning of the rotor at 10 KHz. Aramped 1H pulse was applied during the 1 ms contact time to circumvent Hartmann-Hahn mismatches. A 90° 1H-pulse width of 2.9 µs and ¹³C of 2.79 µs was used for all spectra. The ¹³C chemical shifts were calibrated relative to tetramethylsilane (0 ppm) with glycine (COOH at 176.04 ppm). The spectra were quantified by integration of the following chemical shift regions (Knicker *et al.*, 2008 15; Knicker, 2011 16) using Mestrenova 12.0®, where alkyl C (0–45 ppm); N-alkyl/methoxyl C (45–60 ppm); O-alkyl C (60–110 ppm); aromatic C (110–160 ppm); carbonyl/amide C (160–250 ppm). C and N content were determined by elemental analysis in a Perkin Elmer analyser.

2.3 FTIR

The resultant ICB product and biochar were subjected to FTIR analysis in the range of 400 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 ICB and biochar separately with 0.1% KBr (FT-IR grade, Aldrich Chemical Co., Milwaukee, WI). After grinding, the sample mixture was placed over the top of the micro sample cup and the excess material was removed with a straight edged tool. For the background, a micro sample cup of pure KBr was prepared. The spectra were recorded with Perkin Elmer 1600 FT-IR spectrophotometer fitted with an apparatus to diffuse reflectance. The spectra were recorded with 200 scans collected at 4 cm⁻¹ resolution.

2.4 Incubation and N-fate and Dynamics in Soil

Soil samples (dystrophic Red Ultisols) (EMBRAPA, 2006), were collected at 0 - 20 cm depth under native grassland at the Agronomic Experimental Station of Federal University of Rio Grande do Sul (EEA / UFRGS). The sampling site is situated within the Eldorado do Sul county and located between latitude $30^{0}05$ ′ 22 "S and $51^{0}39$ ′ 08" W. Short-term incubation study was conducted at lab K-104, Institute of Chemistry, Campus Do Vale, UFRGS. The composite soil samples (200 g soil) were weighed into plastic cups and the following treatments (three replicates) were implemented; T1 - control (soil without amendment), T2 - ICB at 75 kg N/ha, T3 - ICB at 145 kg N/ha, T4 - ICB at 290 kg N/ha, T5 - urea at 75 kg N/ha, T6 - urea at 145 kg N/ha, T7 - urea at 290 kg N/ha, T8 BC at 75 kg N/ha, T9 - BC at 145 kg N/ha and T10 BC at 290 kg N/ha. Soil samples were collected for the determination of extractable NH₄⁺ and NO₃⁻ at 1st, 3rd, 7th, 14th, 21st and 28th day after incubation by the Kjehldal method. To 5 g of wet soil sample, weighed in 90 ml snap-cap, 50 mL of 1 M KCl was added and the suspension was mechanically shaken for 30 minutes. The extractant was left overnight decanted and thereafter 20 mL were transferred into a specific bottle for distillation. 5ml of boric acid were used as indicator solution with 0.2 g of MgO and 0.2 g of Devarda alloy were used as catalysts for NH₄⁺ and NO₃⁻. About 35 – 40 ml of the distilled

solution was collected into an Erlenmeyer flask for both determinations. Both solutions were titrated with 0.0025 M H₂SO₄ until the colour change to pink. The concentration of mineral N was calculated according to equation 1.

N mineral
$$\left(\frac{\text{mg}}{\text{kg}}\right) = \frac{(\text{ml H+ sample} - \text{ml H+ blank}) \times 70 \times 2.5}{5 \text{ g}}$$
 (1)

After the completion of incubation study, soil pH was measured in a 1:1 soil-water ratio using a glass electrode (H19017 Microprocessor) pH meter. Approximately 10 g of soil was weighed into a 50 mL beaker and 10 mL of distilled water was added to the soil. The soil-water solution was stirred thoroughly for one minute and allowed to stand for 1 hour. After calibrating the pH meter with buffers of pH 4.01 and 7.00, the pH was determined by immersing the electrode into the upper part of the soil solution and the pH value recorded.

2.5 Humic Substances Distribution

Soil samples were collected at 28th day after incubation to determine chemical fractionation of SOM according to Swift (1996 26) and quantified according to Dick *et al.*, (1998 7). Two grams of wet soil was shaken with 30 ml of 0.5M HCl for 2 hours. The acid extract was separated by centrifugation. The procedure was repeated three times and the final extraction volume was measured. The remaining soil was shaken with 60 ml of 0.5 M NaOH for 2 hours to extract the soluble humic substances (SHS), namely humic acids (HA) and fulvic acids (FA). The same procedure was repeated until the supernatant became colourless and final SHS volume was measured. Aliquots (5 ml) of the acid and of the SHS extracts were collected for further C determination. The pH of the remaining materials was lowered to 2 with 4 M HCl and the suspension was allowed to settle overnight. The precipitated HA was separated from the supernatant soluble FA by centrifugation. The FA extract volume was measured and an aliquot (5 ml) was collected for C determination. The concentration of HA fraction (CHA) was determined as follows (equation 2):

$$C_{HA} = C_{SHS} - C_{FA}$$
(2)

The humification degree were comparatively assessed by the HA/FA ratio.

3. Results and Discussion

The elemental composition of biochar materials before and after intercalation with urea fertilizer are presented in Table 1. Biochar sample contained 40.31 % C, 2.71 % N and 3.34% H hydrogen whereas Intercalated biochar (ICB) contained 28.78 % carbon, 22.04 % N and 4.83 % of hydrogen. The C/N ratio of B (14.87) is usually low for pyrogenic materials and this is probably due to the composition of the biomass that is rich in N compounds and to the low pyrolysis temperature (Jindo, *et al.*, 2020). Total N in intercalated biochar is greater than that in the B (Table 1) as expected, indicating that the incorporation of urea was successful. As a consequence C content relatively decreased and C/N ratio was 1.31. This indicate that the high C : N ratios in the B suggest the relatively low mobilisation of N.

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Sample	C (gkg ⁻¹)	N (gkg ⁻¹)	H (gkg ⁻¹)	C:N	
В	40.31	2.71	3.34	14.87	
ICB	28.78	22.04	4.83	1.31	

Table 1. Elemental composition of biochar (B) and intercalated biochar (ICB)

3.1 Chemical Composition of Biochar and Intercalated Biochar (ICB) Assessed by ¹³C NMR/CPMAS

¹³C-NMR spectra of B and ICB are presented in Figure 1. Distribution of the main chemical groups of C identified in both sample are given in Table 3 The spectra present similar pattern, but differ regarding the abundance of the main C groups. BC showed a predominance of aromatic groups, followed by alkyl C and O-akyl C as expected for low temperature biochar (Cheng *et al.*, 2006; Brewer *et al.*, 2011 6, 5). ICB showed a greater proportion of N/O alkyl C and carbonylic C due to the addition of urea. Also, a greater proportion of O-alkyl C and anomeric C as a result of added starch. Consequently, in ICB the relative proportion of aromatic decreased in comparison to B (Table 3).



Figure 1. The solid state 13C NMR CP/MAS spectra result of biochar pyrolyzed at 400 °C and ICB

The results of physical and chemical properties of soil samples used for the study are presented in Table 2. The textural class of the soil was sandy clay loam and very low pH value of the soil (4.8) which was an indication of an acidic soil (Foth *et al.*, 1990, Esu 2010). It could be attributed to the acidic parent materials (granite) of the soil type (Ultisols) which are known to have low base saturation (Fageria and Baligar, 2008). Low total N (0.63 %), organic carbon (1.5 %) and extremely low available P (3.0 mg kg⁻¹) value revealed the low fertility status of the soil (Adepetu *et al.*, 2014).

Properties			Values
рН (H ₂ O)			4.80
Particle Size			
	Sand	(g kg ⁻¹)	540
	Silt	(g kg ⁻¹)	240
	Clay	(g kg ⁻¹)	220
Textural Class			Sandy clay loam
Carbon content (%)			1.50
CEC (cmol kg ⁻¹)			9.30
Total Nitrogen (%)			0.63
Available P (mg kg ⁻¹)			3.00

Table 2. Physical and chemical properties of the soil sample

	¹³ C NMR CP/MAS - C (%) distribution									
Chemical	0-50	50-65	65-95	95-120	120-150	150-170	170-200	200-		
shift (ppm)								230		
	Alkyl	Nitrosyl	Alcoxides	Anomeric	Aromatic	Aromatic	OC(OH)	CO		
	С			Alcoxides		С				
BC	27.8	3.90	6.90	2.80	48.3	6.10	3.30	0.80		
ICB	22.2	11.8	22.6	7.10	22.6	8.00	2.00	3.80		

Table 3. 13 C NMR CP/MAS – C (%) distribution of biochar and intercalated biochar (ICB)

3.2 FTIR Spectra of Biochar (BC) and Urea-Intercalated Fertilizer (ICB)

The FTIR spectra of BC and ICB are presented in Figures 2 and 3. ICB spectra clearly indicated presence of OH stretch peaks at 3287.5 cm⁻¹ which corresponds to Amine group (34292 - 3332.2 cm⁻¹). An alkyl aromatic group was observed in the BC samples as well as presence of ketone and alcohol groups at 2400 cm⁻¹ 1000 cm⁻¹ respectively. The stretching of the OH from 3700 - 3600 cm⁻¹ and at 2929.7, 2370.6, 2154.4, 2023.9 cm⁻¹ indicate the presence of Alkyl, C – H stretch further confirms the abundance of major functional groups in the BC samples. In the ICB sample, the N-H peaks observed at 3429.2 to 3332.2 cm⁻¹ clearly confirm the presence of the amino (R-NH₂) functional group. In addition, C – O and C – H peaks were observed at regions 1587.8 cm⁻¹, 1148.0 cm⁻¹ respectively as well as alkyl C-H peaks at 2370.6 cm⁻¹. The presence of amine group in the FTIR Spectra of ICB supported NMR result earlier reported. This is an indication of feasibility of intercalating urea with biochar and possibility of slow N release (Manikandan and Subramanian, 2013 18). ICB spectra are composed of alkaloids, carboxylate and ether functional groups while aromatic compound groups dominated BC thus showing the ICB in improving the CEC of the soil and other chemical properties like pH and Total N.



Figure 2. FTIR spectra (4000-500 cm-1) of biochar 400°C



Figure 3. FTIR spectra (4000-500 cm-1) of urea-intercalated biochar

3.3 Distribution of Humic Fractions

Figure 4 illustrates the distribution of humic fractions determined at 28th DAI. In general, the humic fractions proportions did not show any variation for a given treatment within the doses range and values obtained for the treatments did not vary coherently from the control. 3.17 % (U0290) 7.48 % (U75). For C-SH, of the highest value (47.88 %) was observed for U75 and the lowest (26.90 %) for ICB 290. C-HU varied from 67 % (ICB290) 44.64 % (U75).



Figure 4. Distribution of C-HCL, C-SH and C-HU fraction on each treatments

3.4 Effect of Biochar, Urea and ICB on Extractable NH₄-N, NO₃-N and pH in the Soil

Concentration of extractable N-NH₄⁺ were released gradually from urea fertilizer at 145 and 290 kg N ha⁻¹, whereas the ICB at 145 and 290 kg/ha were slower. This justify the ability of ICB to maintain longtime N availability in soils (Preusch *et al.*, 2002 24). Also, the additional carbon from ICB might have stimulated microbial growth and probably enhance immobilization (Lemenih and Karltun 2016 17) which is likely to be responsible for the slow release of N-mineralization. No significant difference (P > 0.05) was obtained between the BC treatments and control over time, expect at the 28 DAI which indicate a significant difference (P < 0.001) between biochar and control. This implies that N-NH₄⁺ was released more at 28 DAI.

The highest N-NH₄⁺ concentrations at 28 DAI were obtained from urea and ICB at 290 kg ha⁻¹, and both treatments differed from control over time. However, N-NH₄⁺ concentration from ICB at 75, 145, and 290 kg ha⁻¹ treatments over time were significantly different from each other. No evidence of extractable N-NO₃⁻ nitrate ion was detected until 14 DAI (Table 4a). Significant difference (P < 0.001) was obtained between ICB and urea over time. Also, significant difference (P > 0.05) was obtained between the ICB and control over time. ICB at 290 kg ha⁻¹ yielded higher extractable nitrate ion concentrations in the soil than all the other treatments at 21 DAI. At 28 DAI, nitrate ion concentration from U at 290 kg ha⁻¹ was greater than what was obtained from all other treatments. The effect of ICB, B and Urea fertilizer on soil pH presented in Table 4c revealed positive significant effect of ICB treatments compared with other treatments. The application of ICB to the soil significantly (P > 0.05) increased the soil pH till 28 DAI. ICB fertilizer applied at 75, 145 290 kg ha⁻¹ significantly increased the soil pH (P < 0.001) at 28 DAI compared to control and urea fertilizer. Among the employed treatments only those with ICB and BC increased the soil pH.

Nitrate (NO ₃ -)											
TRT	CON	ICB75	ICB145	ICB290	U75	U145	U290	BC75	BC145	BC290	
DAY	NO3⁻ (mg/kg)								→		
1	nd	nd	nd	Nd	nd	nd	nd	nd	nd	nd	
3	nd	nd	nd	Nd	nd	nd	nd	nd	nd	nd	
7	nd	nd	nd	Nd	nd	nd	nd	nd	nd	nd	
14	7.66	15.28	17.55	19.47	9.19	10.08	19.11	7.48	8.95	11.19	
14	cA	abA	aC	aC	cВ	cВ	aB	cA	cA	bcA	
21	5.45	20.6	24.21	27.79	8.37	13.52	22.64	4.93	8.11	13.55	
21	dA	abA	aB	aB	cdA	bcB	aB	dBC	cdA	bcA	
20	5.78	25.28	30.06	36.2	23.14	33.36	50.93	8.89	10.59	13.07	
28	gA	deA	cdA	bA	eA	bcA	aA	fA	fA	fA	

Table 4a. Effect of the treatments with time on Nitrate

Mean values with the same small and capital letters in a row and column, respectively are not significantly different at probability level of 0.05. N.d (not detected). CON = Control; ICB 75, ICB 145 and ICB 290 = intercalated biochar at rates 75, 145 and 290 kg N/ha, respectively; U75, U145 and U290 = urea at rates 75, 145 and 290 kg N/ha, respectively; B75, B145 and B290 = Biochar only at rates 75, 145 and 290 kg N/ha, respectively.

Ammonium (NH₄⁺)

TRT	CON	ICB75	ICB145	ICB290	U75	U145	U290	BC75	BC145	BC290
DAY		◀			⁻ NH4 ⁺ (m	g/kg)				→
1	27.57	33.79	30.79	33.26	32.84	33.37	35.69	29.62	29.35	31.99
1	aA	aA	aA	aAB	aA	aBC	aA	aA	aB	aB
2	17.02	24.33	18.77	28.3	28.49	51.36	74.07	12.98	13.11	14.21
3	bcB	bcB	bcB	bcAB	bcAB	abA	aA	cBC	cCD	cD
7	11.04	18.14	18.06	20.31	13.04	9	48.33	4.97	5.47	5.34
/	bB	bC	bB	bB	bC	bD	aA	bD	bD	bE
14	15.75	17.12	17.94	24.29	18.8	24.29	59.78	11.29	14.49	16.4
14	bB	bC	bB	bB	bBC	bCD	aA	bCD	bCD	bCD
21	12.14	20.37	22.13	20.31	9.83	16.58	84.65	11.35	10.9	21.57
21	bB	bB	bBC	bC	bC	bCD	aA	bD	bC	bB
20	15.75	32.85	41.65	61.68	19.25	41.05	82.32	21.45	32.06	42.32
28	eB	cdA	cA	bA	eBC	cAB	aA	deBC	cdA	cA

Table 4b. Effect of the treatments with time on Ammonium

Mean values with the same small and capital letters in a row and column, respectively are not significantly different at probability level of 0.05. N.d (not detected). CON = Control; ICB 75, ICB 145 and ICB 290 = intercalated biochar at rates 75, 145 and 290 kg N/ha, respectively; U75, U145 and U290 = urea at rates 75, 145 and 290 kg N/ha, respectively; B75, B145 and B290 = Biochar only at rates 75, 145 and 290 kg N/ha, respectively.

Table 4c. Effect of the treatments with	time on p	Н
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TRT	CON	ICB75	ICB145	ICB290	U75	U145	U290	BC75	BC145	BC290
DAY					pŀ	I				
20	4.8	5.67	5.77	5.99	4.52	4.58	4.54	5.2	5.1	5.12
28	bcd	abc	ab	а	cd	cd	cd	cd	d	d

Mean values with the same small and capital letters in a row and column, respectively are not significantly different at probability level of 0.05. N.d (not detected). CON = Control; ICB 75, ICB 145 and ICB 290 = intercalated biochar at rates 75, 145 and 290 kg N/ha, respectively; U75, U145 and U290 = urea at rates 75, 145 and 290 kg N/ha, respectively; B75, B145 and B290 = Biochar only at rates 75, 145 and 290 kg N/ha, respectively.

4. Conclusions

The spectra of NMR and FTIR of ICB revealed the presence of Amine and N/O-Alkyl functional groups which are not visible in biochar alone. This was an indication that N can be easily adsorbed on biochar particles through intercalation process. Similarly, presence of aliphatic and carboxylic compounds were observed in the spectra of ICB compared to BC. Thus, giving it a dual advantage in improving the CEC of the soil and also make the carbon available for microorganisms. Higher soil pH in ICB treated pots was an indication its potential as liming materials. The rate at which NH_4^+ -N and NO_3 -N release from ICB in a stepwise form indicates that ICB is a slow release fertilizer.

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