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Value of Functionalized Charcoal for Increasing the Efficiency of Urea N Uptake: Insights into the Functionalization Process and the Physicochemical Characteristics of Charcoal

Diogo Mendes de Paiva(1)*, **Gelton Geraldo Fernandes Guimarães**(2), **Breno Cardoso Teixeira**(1) **and Reinaldo Bertola Cantarutti**(3)

(1) Universidade Federal de Viçosa, Departamento de Solos, Programa de Pós-Graduação em Solos e Nutrição de Plantas, Viçosa, Minas Gerais, Brasil.
(2) Empresa de Pesquisa Agropecuária e Extensão Rural de Santa Catariana, Itajaí, Santa Catarina, Brasil.
(3) Universidade Federal de Viçosa, Departamento de Solos, Viçosa, Minas Gerais, Brasil.

ABSTRACT: Functionalized charcoal (CHox) incorporated into urea is known for its ability to reduce NH_3 volatilization and increase agronomic efficiency. However, it is important to optimize the functionalization process and to elucidate its relationship with the physicochemical properties of CHox for N supply. Thus, charcoal obtained from eucalyptus wood was functionalized with different HNO_3 concentrations and reaction times. Ammonia adsorption by CHox was evaluated in chambers with high NH_3 concentrations. Dry matter yield, N uptake, and apparent N recovery efficiency of corn plants were evaluated after the application of the urea-CHox mixture to soil in a greenhouse experiment. The properties of CHox, such as pH, isoelectric point, and total acidity (carboxylic and phenolics groups) depended on the HNO_3 concentration but were not influenced by the reaction time. The NH_3 adsorption by the functionalized charcoal showed a positive correlation with the quantity of carboxylic and phenolic groups and a negative correlation with the pH value and the isoelectric point. The small differences observed in dry matter yield, N accumulation, and apparent N recovery efficiency among the corn plants from urea mixed with CHox or humic acids derived from charcoal (AH_{CH}) are not sufficient to determine the higher efficiency of these sources.

Keywords: biochar, NH_3 adsorption, NH_3 volatilization, efficient fertilization.

*** Corresponding author:**
E-mail: paivadmendes@gmail.com

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INTRODUCTION

Urea is the main nitrogen (N) fertilizer used in crop fertilization in Brazil. However, the agronomic efficiency of urea is low due to N losses via NH_3 volatilization. Currently, there are major research efforts to develop new technologies for the production of more sustainable fertilizers (Lahr et al., 2016; He et al., 2017).

In this context, urea mixed with substances with high acid buffer capacity, such as functionalized charcoal, has shown potential for decreasing ammonia volatilization (Paiva et al., 2012; Guimarães et al., 2015). Functionalized charcoal by HNO_3 is predominantly hydrophilic, and a large part of its functional groups contains oxygen. This facilitates the production of a material that behaves as a base or acid and has ion exchange properties, increasing its potential as adsorbent of heavy metals, organic molecules, and gases (Liu et al., 2007; Shafeeyan et al., 2010; Troca-Torrado et al., 2011).

Paiva et al. (2012) have promoted the functionalization of charcoal by oxidizing it with HNO_3, followed by the separation of fractions according to the methodology of the International Society of Humic Substances (Swift, 1996). With this amendment, coating urea reduces the volatilization of NH_3 by approximately 50 % compared to uncoated urea. In sequence, Guimarães et al. (2015) have observed a 40 % reduction in volatilization by using functionalized charcoal obtained according to Paiva et al. (2012), but without the separation of fractions. Both authors concluded that the volatilization of $N\text{-}NH_3$ from urea can be controlled with substances that have a high CEC (Charge Exchange Capacity), which do not only enhance NH_4^+ retention formed by urea hydrolysis but also contribute to the buffering capacity, thereby moderating the pH increase caused by hydrolysis.

Given the above, it is important to know the best combination of HNO_3 concentration and reaction time for obtaining the functionalized charcoal. According to Boehm (2002), this binomial (HNO_3 concentration *vs.* reaction time) determines the oxidizing power of HNO_3, which is highest with the acid heated to boiling. However, the concentration of HNO_3 and the reaction time to optimize the process of obtaining functionalized charcoal as well as its physicochemical properties are still unknown.

Thus, the objective of this work was to study the influences of HNO_3 concentration and reaction time on the physicochemical properties of charcoal and to evaluate the ability of urea-functionalized charcoal to retain NH_3 and to provide N to corn plants.

MATERIALS AND METHODS

Production of functionalized charcoal

Charcoal (CH) was obtained from *Eucalyptus grandis* wood blocks carbonized in a laboratory oven at 350 °C in the presence of O_2. This temperature was attained in 4 h (following a constant heating rate until obtaining the final temperature of 350 °C) and was maintained for 4 h, resulting in 8 h of carbonization. The temperature was monitored by a thermostat wrapped around the wood. The charcoal was crushed in an ultracentrifugal mill until its granulometry was less than 149 µm and was then dried at 105 °C for 12 h.

Nine CHox were obtained using the HNO_3 concentrations of 0.5, 1.7, 4.5, 7.3, and 8.5 mol L^{-1} and reaction times of 0.5, 1.5, 4.0, 6.5, and 7.5 h, according to the experimental central compound matrix ($2^k + 2k + 1$) and describe CHox1, CHox2, CHox3, CHox4, CHox5, CHox6, CHox7, CHox8, CHox9 in according the table 1. The central point of the matrix was defined by the concentration of 4.5 mol L^{-1} and a reaction time of 4 h, which were used by Paiva et al. (2012) with two replicates.

For the production of the each CHox, 50 g of CH and 1 L of HNO_3, with the respective concentrations, were mixed, heated to boiling, and kept under reflux at the respective

Table 1. Carbon, H, N, and O contents of the nine functionalized charcoals (CHox) obtained according to the concentration of nitric acid and the reaction time of the humic acid obtained from charcoal (AH_{CH}) and eucalyptus charcoal (CH) as raw materials

CHox	HNO_3	Time	C	H	N	O	C/N[1]
	mol L^{-1}	h	%				
1	1.7	1.5	61.87	3.13	2.60	32.40	27.75
2	1.7	6.5	59.79	3.00	2.75	34.46	25.35
3	7.3	1.5	55.81	3.01	3.23	37.95	20.15
4	7.3	6.5	55.90	3.05	3.18	37.87	20.50
5	0.5	4.0	65.88	3.15	2.84	28.13	27.05
6	8.5	4.0	54.70	2.96	3.39	38.95	18.82
7	4.5	0.5	58.60	3.08	3.69	34.63	18.52
8	4.5	7.5	56.17	3.03	3.28	37.52	19.97
9	4.5	4.0	56.39	3.01	3.79	36.81	17.35
Average			58.35	3.05	3.19	35.41	21.72
Confidence level (95 %)			±1.76	±0.03	±0.20	±1.67	±1.90
AH_{CH}	4.5	4.0	52.80	3.19	2.91	41.62	21.16
CH			78.42	3.71	0.05	17.82	1,829.04

(1) Molar ratio. C, H, and N were determined by combustion in an elemental analyzer (Perkin Elmer 2400 Series II CHNS/O), and oxygen was determined by the difference between the initial mass and the C, H, N, and ash contents.

reaction times. At the end of each period, the mixtures were kept at rest for 12 h at room temperature and subsequently slowly filtered through a filter paper under vacuum; the retained material was transferred to cellophane bags where it underwent dialysis in distilled water. The water was changed twice daily until the increase in conductivity 1 h after the replacement was lower than 1 µS cm^{-1} (Benites et al., 2005). After dialysis, the CHox samples were dried at 60 °C, weighed, and ground to obtain a granulometry less than 149 µm; subsequently, they were stored in a desiccator.

We also produced a compound according to the method described in Paiva et al. (2012) to obtain humic acids from CH (AH_{CH}), following the methodology described to obtain CHox of the central point of the matrix previously related. This compound was applied to the extraction of fulvic acids, humic acids, and humins, using the extraction procedure of the International Society of Humic Substances, according to Swift (1996). For this, the material retained in the filter was added to a solution of NaOH 1 mol L^{-1} until a pH of 12.0 was obtained and left to stand for 12 h. Subsequently, the pH of the mixture was adjusted to about 2.0 with H_2SO_4, and the mixture was kept at room temperature for 12 h and subsequently centrifuged at 3,345 *g* for 30 min; the supernatant was discarded. The decanted material was resolubilized in 500 mL of NaOH 1.0 mol L^{-1}, held for 4 h, re-acidified, and centrifuged as previously described. The supernatant was discarded, and the decanted material (AH_{CH}) was transferred to cellophane paper bags where it was dialyzed with distilled water as described above. Subsequently, the AH_{CH} was dried at 60 °C, crushed to a granulometry of less than 149 µm, and stored in a desiccator.

Characterization of functionalized charcoal

The contents of C, H, and N were determined by combustion in an elemental analyzer (Perkin Elmer 2400 Series II CHNS/O), and oxygen was determined by the difference between the initial mass and the C, H, N, and ash contents. The atomic ratio of C/N was determined.

The isoelectric point of CHox and AH_{CH} was determined by mass titration, according to Noh and Schwarz (1989). For the quantification of total acidity, which characterizes the potential cation exchange capacity (CEC), acid-base potentiometric titration was performed to quantify carboxylic and phenolic functional groups, according to Inbar et al. (1990) and Bowles et al. (1989).

Photoelectric X-ray spectroscopy (XPS) was performed in a VSW HA-100 spherical analyzer using an aluminum anode (Al Kα, hv = 1486.6 eV). The constant passage of incident energy was 44 eV, in a fixed transmission mode providing a line width of 1.6 eV of Au 4f 7/2. The pressure employed during the analysis was less than 2×10^{-8} mbar. To correct the binding energies, the C 1s line with the binding energy of 284.6 eV was used as reference. Qualitative interpretation of the spectra was performed according to Abe et al. (2000).

Adsorption of NH_3 by functionalized charcoal

The adsorption capacity of NH_3 by CHox and AH_{CH} was evaluated in chambers with high concentrations of NH_3. The chambers were made of 300 cm^3 glass vials with internal support to hold the Petri dishes containing 1 g of each of the nine CHox and AH_{CH} samples. Inside the chambers, 10 mL of 0.3 mol L^{-1} $(NH_4)_2SO_4$ were placed, and the chambers were hermetically sealed. Subsequently, 10 mL of 0.67 mol L^{-1} NaOH were injected into the chambers through a rubber-sealed hole. For alkalinization, a high concentration of NH_3 was provided.

The samples remained in the chamber for 7 days in a temperature-controlled environment at 25 °C (± 2 °C). After this period, 10 mL of H_2SO_4 0.3 mol L^{-1} were added to each chamber, and after 2 h, the chambers were opened. The Petri dishes with the samples were transferred to an oven at 30 °C and kept there for 24 h. Subsequently, the N content was determined with an elemental analyzer (Perkin Elmer 2400 Series II CHNS/O Analyzer). Adsorbed N-NH_3 was estimated by the difference between the N contents after and before incubation. Evaluations were performed based on three replicates of each sample.

Supply of N from Urea-CHox

A greenhouse experiment was carried out using urea mixtures with CHox6 (U-CHox6), CHox9 (U-CHox9), and AH_{CH} (U-AH_{CH}) in a proportion of 500 g kg^{-1}, as well as urea and NH_4NO_3, applied at four N doses (0, 90, 180, and 270 mg dm^{-3}) to evaluate N supply to corn plants (*Zea mays* L.). According to table 1, CHox6, CHox9, and AH_{CH} represent the functionalized charcoal; NH_4NO_3 was used as a reference N fertilizer without N-NH_3 volatilization. The experiment was arranged in randomized blocks with four replicates. Samples of the 0.00-0.20 m layer of an air-dried Oxisol (Typic Hapludox/*Latossolo*) were used, with particle size less than 2 mm and the following characteristics: pH(H_2O) 4.6, measured with a glass electrode; organic carbon of 12.5 g dm^{-3}, measured by the Walkley-Black method according to Nelson and Sommers (1996); 2.3 mg dm^{-3} of available P (Mehlich-1) according to Oliveira et al. (1979); 21 mg dm^{-3} of available K, according to Embrapa (1979); Ca, Mg, and Al contents of 0.17, 0.05, and 0.92 $cmol_c$ dm^{-3}, respectively, according to Embrapa (1979); residual remaining phosphorus (P-rem) of 9 mg L^{-1} according to Alvarez et al. (2000); and potential acidity (H+Al) of 6.4 $cmol_c$ dm^{-3}, according to Oliveira et al. (1979).

The soil was limed to neutralize Al, and the levels of Ca+Mg were raised to 2 $cmol_c$ dm^{-3} with the application of 2.0 g dm^{-3} of a mixture of $CaCO_3$+$MgCO_3$ in the molar ratio of 3:1, reaching a pH of 6.0 after soil incubation. The experimental units consisted of plastic pots containing 2.5 dm^3 of soil and five early maturing hybrid corn plants. Sowing was performed after soil fertilization with 300 mg dm^{-3} of P, 150 mg dm^{-3} of K, 40 mg dm^{-3} of S, 0.81 mg dm^{-3} of B, 1.33 mg dm^{-3} of Cu, 1.55 mg dm^{-3} of Fe (as Fe-EDTA), 3.66 mg dm^{-3} of Mn, 0.15 mg dm^{-3} of Mo, and 4 mg dm^{-3} of Zn. The nutrient doses, including N, were defined according to Novais et al. (1991). The N doses, according to the treatment, were applied at 30 days after emergence (stage of high nutrient demand) by locating the fertilizer on the soil in the central part of the pot surface. The moisture content of the soil was maintained close to 70 % by applying distilled water periodically on the soil surface.

After 60 days of growth (stage of flowering), the plants were cut 1 cm above the ground. The plant material was dried (65 °C for 72 h), ground, and the N content was determined by Kjeldahl digestion and distillation, according to Bremner and Mulvaney (1982). Based on the accumulated dry mass and N content, the accumulated N content was estimated, and thus, the apparent N recovery efficiency was estimated using equation 1:

$$\textit{Apparent N recovery index } (\%) = \frac{N1 - N0}{\textit{total N applied}} \times 100 \qquad \text{Eq. 1}$$

in which *N1* refers to the N content in the corn plants in each dose of N applied and *N0* refers to the N content in the corn plants at an N dose of zero.

Statistical analysis

The potentiometric characterization and NH_3 adsorption data of the functionalized charcoal were submitted to variance analysis. Regression equations were adjusted according to the complete model: $\hat{y} = \beta0 + \beta1\ t + \beta2\ t2 + \beta3\ H + \beta4\ H2 + \beta5\ tH + \mathcal{E}$, where “H” is the concentration of HNO_3 in mol L^{-1} and “t” is the reaction time in hours. The effects of these factors were evaluated by the significance of the regression coefficients at $p<0.10$.

The average values of N adsorbed by each treatment were submitted to contrast analyses among treatments. Also, the values of N adsorbed were submitted to the linear correlation of variable responses.

Dry matter yield, N uptake, and apparent N recovery efficiency values were submitted to variance analysis, and the effects of the treatments were compared through regression, with the coefficients of the equations being based on the mean square of the residue of the analysis of variance at $p<0.10$. Also, averages of dry matter yield and N uptake were compared for each N dose by Tukey’s test ($p = 0.05$).

The package Minitab Statistical Software 14 (Minitab Inc., State College, Pennsylvania, US) was used to carry out all analyses.

RESULTS

Characterization functionalized charcoal

Functionalization with HNO_3 promoted an increase up to 75 times in the N and up to 2.2 times in the O content of CHox and AH_{CH}, while the amount of C decreased with respect to CH (Table 1). The AH_{CH} showed a higher O content than CHox, while the contents of C and N were higher for CHox. The pH of CH in water was 5.86, while that of AH_{CH} was 3.56 and that of CHox ranged from 2.73 to 3.25 (Table 2). The isoelectric points indicate that the positive and negative charges in the compounds are balanced at a pH between 1.57 and 2.08, while for charcoal, the PI was 6.06, being higher than its pH in water (Table 2).

The pH of CHox was influenced only by the concentration of HNO_3, as shown by the adjusted regression equation (Table 3). The isoelectric point, however, was neither significantly influenced by the concentration of HNO_3 nor by the reaction time, corresponding to a mean value of 1.68 (Table 2).

The total acidity of AH_{CH} was 11 times higher than that of CH, while the total acidity of CHox was between 5.7 and 12.9 times higher than that of CH (Table 2). For CHox, the carboxyl groups presented a total acidity of 59 to 74 %, while for AH_{CH}, total acidity was 76 %, based on the data presented in table 2. The carboxyl group content of the CHox

Table 2. Isoelectronic points (PI), pH values in water, quantity of carboxylic groups, phenolics, and total acidity values of the functionalized charcoals (CHox) obtained according to nitric acid concentration and reaction time of humic acid obtained from charcoal (AH_{CH}) and eucalyptus charcoal (CH)

CHox	HNO_3	Time	$pH(H_2O)^{(1)}$	$PI^{(2)}$	$Carboxylic^{(3)}$	$Phenolic^{(3)}$	$Total^{(4)}$
	mol L^{-1}	h				mmol$_c$ kg^{-1}	
1	1.7	1.5	2.97	1.68	1,671	1,157	2,828
2	1.7	6.5	2.91	1.66	2,216	1,266	3,482
3	7.3	1.5	2.81	1.57	2,970	1,516	4,486
4	7.3	6.5	2.73	1.59	3,381	1,148	4,529
5	0.5	4.0	3.25	2.08	1,263	884	2,147
6	8.5	4.0	2.84	1.62	3,616	1,269	4,885
7	4.5	0.5	2.88	1.67	2,081	1,387	3,468
8	4.5	7.5	2.82	1.62	3,435	1,400	4,835
9	4.5	4.0	2.79	1.64	3,134	1,407	4,541
Average			2.89	1.68	2,641	1,271	3,911
Confidence level (95 %)			±0.12	±0.10	±586	±131	±671
AH_{CH}			3.56	1.64	3,214	1,008	4,222
CH			5.86	6.06	251	126	377

(1) Solid:solution ratio of 1:10. (2) PI obtained by mass titration. (3) Estimated by potentiometric titration, from the titrant volumes to raise the pH from 3 to 8 (carboxylic) and from 8 to 10 (phenolics). (4) Sum of the contents of carboxylic and phenolic groups.

Table 3. Regression equations adjusted to pH in water and functional groups contents according to the concentration of HNO_3 (H) and reaction time (t) expressed in hours

pH and content of functional groups	Regression equation	R^2
$pH(H_2O)$	$\hat{y} = 3.29 - 0.158^{***}H - 0.011\ t + 0.013^{***}H^2$	0.88
Carboxylic	$\hat{y} = 1531.4 + 257.4^{***}H$	0.70
Phenolics	$\hat{y} = 901.3 + 212.4^{**}H - 12.2\ t - 19.7^{**}H^2$	0.74
Carboxylic + Phenolics	$\hat{y} = 2658.2 + 292.4^{***}H$	0.68

*** Significant at p<0.01; ** significant at p<0.05.

increased linearly with the concentration of HNO_3, while the contents of phenolic groups increased in a quadratic manner (Table 3). Considering the prevalence of carboxylic groups, total acidity also increased linearly, reaffirming the irrelevance of the reaction time (Table 3).

Characteristic peaks of carboxylic, phenolic, and ether groups were identified in the surface structure of the compounds evaluated (Table 4). For CHox, the C identified between 9 and 14 % is attributed to carboxylic groups, whereas for AH_{CH}, this ratio was 15 % and for CH, it was only 5 %. The relative proportion of C, based on C 1s spectra, associated with phenolic groups or ether for CHox, varied between 13 and 24 %; for AH_{CH}, it was 16, whereas it was 15 % for CH. The structures described based on C 1s spectra are confirmed with the spectra obtained for O 1s (Table 4), with the identification of peaks related to C=O bonds, which may represent carboxylic acids and aromatic bonds of O and C (CAr) of phenols or ether. There was a lower amount of O-CAr in both CHox and AH_{CH} than in CH, agreeing with the previous assertion that there is a reduction in the amount of ether groups with the formation of carboxylic groups after functionalization with HNO_3.

The O 1s spectra results indicate greater similarity between CHox and AH_{CH}. However, the XPS analysis of O was less conclusive than for C, since the identification of these types of bonds may relate to more than one functional group, for example, C=O for carboxylic or aldehydes (Abe et al., 2000). The N 1s spectra revealed only two absorption peaks, with

Table 4. Relative proportions of the surface chemical species of C, O, and N, identified by the XPS spectra of C 1s, O 1s, and N 1s, respectively, in CHox according to the concentration of HNO_3 and the reaction time, for humic acids obtained from charcoal (AHc_H) and eucalyptus charcoal (CH)

CHox	HNO_3	Time	Aromatic or aliphatic C	Carboxylic groups	Phenolic or ether groups	O bound to aromatic C	C=O	N pyrrol pyridine or amines	NO_2 groups/ oxidized nitrogen functions
	mol L^{-1}	h				%			
1	1.7	1.5	76	9	15	55	43	65	35
2	1.7	6.5	54	10	24	39	49	59	41
3	7.3	1.5	68	13	16	49	51	49	51
4	7.3	6.5	66	10	13	48	49	51	49
5	0.5	4.0	68	10	19	37	60	69	31
6	8.5	4.0	70	14	13	48	43	51	49
7	4.5	0.5	73	10	17	48	52	79	21
8	4.5	7.5	63	13	24	50	50	59	41
9	4.5	4.0	71	13	16	50	50	68	32
Average			71.5	16.5	12.0	69.5	30.5	71.5	28.5
Confidence level (95 %)			±0.9	±0.9	±1.9	±38.2	±35.7	±6.8	±5.9
AH_{CH}			69	15	16	49	51	52	38
CH			80	5	15	74	26	-	-

one of them being related to C-N-C type bonds, which could be attributed to N insertion into an aromatic C structure (pyrrole or pyridone), with the formation of amines (Table 4).

Adsorption of NH_3 by functionalized charcoal

Table 5 shows the adsorption of NH_3 on the surface of the charcoals. The AH_{CH} adsorbed 5.9 times more N-NH_3 than CH, whilst CHox, with the exception of CHox5, presented a 3 to 9 times higher adsorption than CH. The highest correlation observed was with the carboxylic groups (Table 6), indicating that its greater presence favors adsorption compared to the presence of phenolic groups. These results were confirmed through the lower correlation and the significance observed for NH_3 adsorption on phenolic groups. The pH and PI also showed a correlation with N-NH_3 adsorption, indicating that lower pH and PI values favor NH_3 adsorption on CHox.

Due to the better result showed by CHox6 in terms of NH_3 adsorption, this functionalized charcoal was selected from the matrix (Table 1) to evaluate its interaction with urea in a plant fertilization experiment. In addition to CHox6, the centre point of the matrix “CHox9” was evaluated and represented the functionalized charcoal under the same conditions as described in Paiva et al. (2012) and Guimarães et al. (2015).

Supply of N from Urea-CHox

The corn fertilized with urea had a lower rate of dry matter accumulation as a function of the N dose than corn fertilized with other fertilizers, as shown by the linear coefficients of the regression equations (Figure 1). The linear coefficients of the equations for U-CHox6, U-CHox9, and U-AH_{CH} were greater or close to those adjusted for the response to NH_4NO_3, indicating that the responses of corn plants fertilized with urea combined with CHox or AH_{CH} could be equivalent to the response to NH_4NO_3. The levels of N accumulated in the corn shoots of the corn plants increased linearly with the N rates for all fertilizers (Figure 2). The highest increase in accumulated N was verified for NH_4NO_3, while urea and U-CHox6 had the lowest rates. However, U-CHox9 and U-AH_{CH} presented lower increase rates than NH_4NO_3, but 8 and 13 % higher rates, respectively, than those estimated for urea.

Table 5. The N-NH_3 adsorbed by functionalized charcoals (CHox) produced according to the concentration of HNO_3 and the reaction time, for the humic acid obtained from charcoal (AH_{CH}) and eucalyptus charcoal (CH), and the average contrasts between the amounts of N adsorbed in treatments associated with statistical significance

CHox	HNO_3	Time	N-NH_3 adsorbed
	mol L^{-1}	h	mg g^{-1}
1	1.7	1.5	18.50
2	1.7	6.5	19.70
3	7.3	1.5	35.23
4	7.3	6.5	41.87
5	0.5	4.0	5.53
6	8.5	4.0	53.53
7	4.5	0.5	43.23
8	4.5	7.5	55.87
9	4.5	4.0	48.57
AH_{CH}			36.80
CH			6.17
Average			33.18
Confidence level (95 %)			6.18
Average contrast			
C1 = - CH vs (CHox1+CHox2+ ... +CHox9)			26.65*
C2 = - CH vs AH_{CH}			3.06*
C3 = - CHox vs AH_{CH}			-0.89^{ns}
C4 = - CHox5 vs (CHox1+CHox2+ ... +CHox9)			27.69*

* Significant at $p<0.05$. ^{ns}: not significant.

Table 6. Coefficients of linear correlation between N-NH_3 adsorption (mg g^{-1}) and the quantity of carboxylic groups ($mmol_c$ kg^{-1}), or quantity of phenolics groups ($mmol_c$ kg^{-1}), or pH value, or isoelectronic point (PI) values

Physical-chemical properties	Coefficient
Carboxylic groups	0.88***
Phenolics groups	0.68**
pH	- 0.80***
PI	- 0.70**

*** Significant at $p<0.01$; ** significant at $p<0.05$.

For equivalent N doses required to reach 90 % of the estimated maximum yield for NH_4NO_3, a 34 % higher dose for urea was required, whereas for U-CHox6 and U-CHox9, the doses would be 1 and 11 % lower, respectively, and for U-AH_{CH}, the dose would be 7 % higher (Table 7). The lower efficiency of urea is also evidenced in the equivalent N dose to reach 80 % of the accumulated N content in relation to the corn plants fertilized with NH_4NO_3, in that there is a need for a 30 % higher N dose (Table 7). For U-CHox6, the required dose should be 40 % higher, and for U-CHox9 and U-AH_{CH}, these doses would be 15 and 20 %, respectively, higher in relation to the dose of N applied as NH_4NO_3.

By evaluating the means of dry matter yield and N uptake within each dose (Table 8), corn plants fertilized with U-CHox9 and U-AHCH showed statistically higher dry matter yields at the N dose of 180 mg dm^{-3} and equivalence in the N content at 270 mg dm^{-3} of N to NH_4NO_3. Although the N content at this dose is still equivalent to that observed

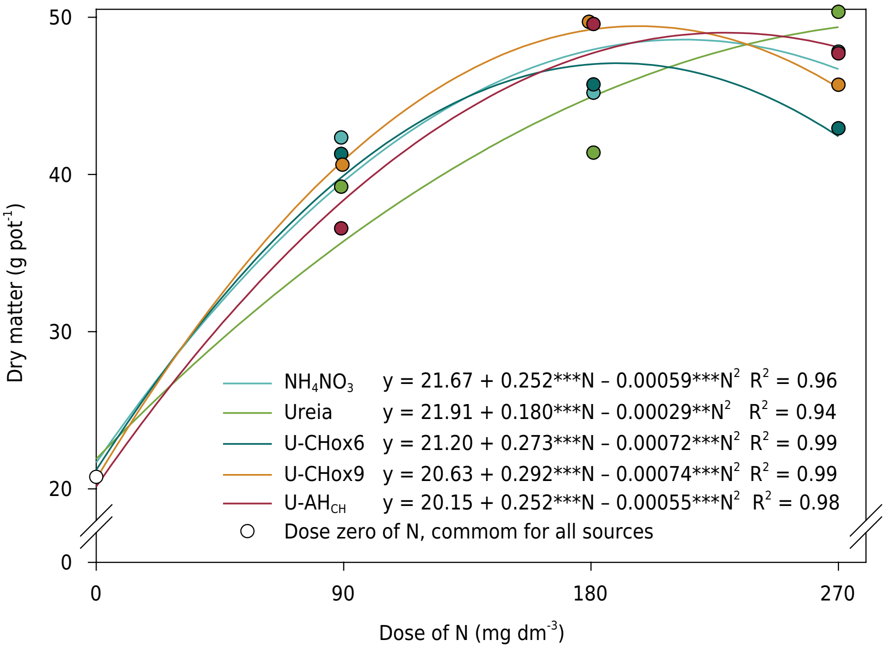

Figure 1. Dry matter yield of corn plants as a function of N dosages applied as NH_4NO_3, urea, and urea mixed with functionalized charcoals (U-CHox6 or U-CHox9) or humic acids derived from CHox (U-AH_{CH}). Equations representing the observed values are shown for $p<0.01$ (***) and $p<0.05$ (**).

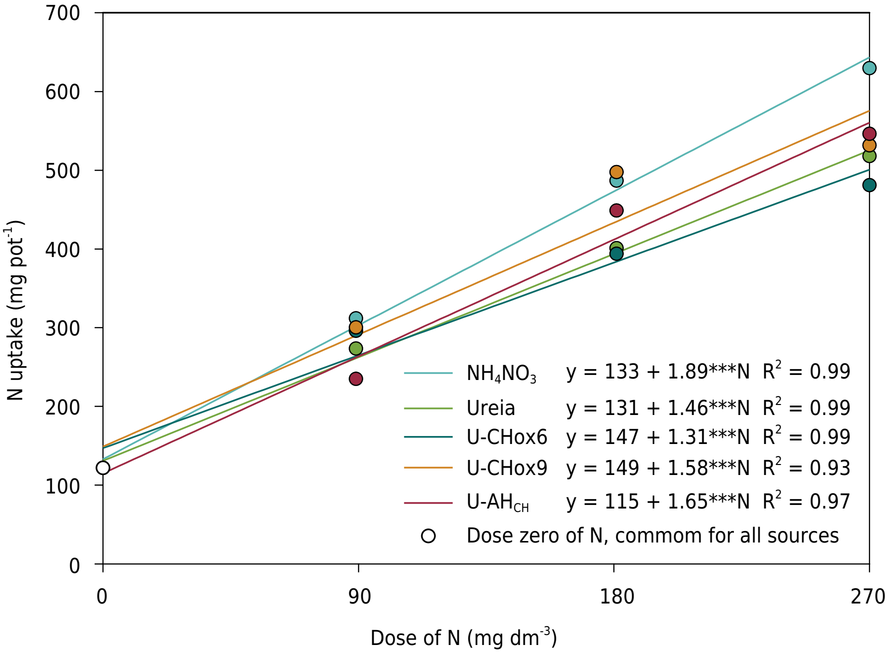

Figure 2. Nitrogen uptake by corn plants as a function of N dosages applied as NH_4NO_3, urea, and urea mixed with functionalized charcoals (U-CHox6 or U-CHox9) or humic acids derived from functionalized charcoals (U-AH_{CH}). Equations representing the observed values are shown for $p<0.01$ (***).

for urea, the fact that it is statistically equal to NH_4NO_3 indicates the greater potential of these sources in providing N when compared to urea.

The apparent N recovery efficiency of corn plants was between 75.22 and 84.30 % when fertilized with NH_4NO_3 (Table 9), while for other fertilizers, it was between 50.21 and 83.48 %. However, among fertilizers, the apparent N recovery efficiency was statistically equal (Table 9), and in each fertilizer, statistical difference was only found among doses to U-AH_{CH} and NH_4NO_3.

Table 7. Nitrogen dose to reach 90 % of maximum dry matter (DM) yield and 80 % of the highest amount of N absorbed. Values estimated from the adjusted regression equations for DM yield and N absorbed of corn as a function of N dosages applied as NH_4NO_3, urea, urea mixed with oxidized charcoals (U-CHox6, U-CHox9) or humic acids derived from CHox (U-AH_{CH})

Fertilizer	N dose	
	90 % of maximum DM yield	80 % of maximum N absorbed
	mg dm^{-3}	
NH_4NO_3	122.85	201.93
Urea	165.10	262.77
U-CHox6$^{(1)}$	121.30	280.64
U-CHox9$^{(1)}$	109.40	231.42
U-AH_{CH}	131.00	242.21

$^{(1)}$ Mixture of urea with oxidized carbon CHox in the proportion of 500 g kg^{-1}.

Table 8. Dry matter yield and N uptake by corn plants for each N dosage applied as NH_4NO_3, urea, and urea mixed with functionalized charcoals (U-CHox6 or U-CHox9) or humic acids derived from CHox (U-AH_{CH})

Fertilizer	N dose					
	90 mg dm^{-3}	180 mg dm^{-3}	270 mg dm^{-3}	90 mg dm^{-3}	180 mg dm^{-3}	270 mg dm^{-3}
	Dry matter yield			N uptake		
	g pot^{-1}			mg pot^{-1}		
NH_4NO_3	42.34 a	45.20 ab	47.81 a	311.55 a	486.84 a	629.61 b
Urea	39.22 a	41.38 a	50.34 a	273.30 a	400.99 a	517.96 ab
U-CHox6$^{(1)}$	41.30 a	45.72 ab	42.94 a	295.82 a	393.89 a	401.05 a
U-CHox9$^{(1)}$	40.62 a	49.71 b	45.70 a	300.28 a	497.55 a	531.51 ab
U-AH_{CH}	36.57 a	49.56 b	47.70 a	234.86 a	448.85 a	546.14 ab

$^{(1)}$ Mixture of urea with oxidized carbon CHox in the proportion of 500 g kg^{-1}. Means followed by the same letter in a column are not significantly different according to Tukey's test (p=0.05).

Table 9. Apparent N recovery by corn plants according to the doses of NH_4NO_3, urea, and urea mixed with the functionalized charcoals (U-CHox6 or U-CHox9) or humic acids derived from CHox (U-AH_{CH})

Fertilizer	N dose		
	90 mg dm^{-3}	180 mg dm^{-3}	270 mg dm^{-3}
	Apparent N recovery		
	%		
NH_4NO_3	84.30 A b	81.10 A a	75.22 A a
Urea	67.30 A ab	62.03 A a	58.68 A a
U-CHox6^1	77.31 A ab	60.45 A a	53.21 A a
U-CHox9^1	79.29 A ab	83.48 A a	60.69 A a
U-AH_{CH}	50.21 A a	72.66 A a	62.85 A a

Means followed by the same small letters in a line and capital letters in a column are not significantly different according to Tukey's test (p=0.05).

DISCUSSION

The results of the elemental analyses (Table 1) indicate an increase in the amount of O with the reduction of the amount of C in the CHox and AH_{CH}, evidencing the functionalization effect of HNO_3 on CH, providing the formation of functional groups. Also, we assume that AH_{CH} are more saturated than CHox, suggesting that the separation of the alkaline soluble material favors AH_{CH}. The increase in aliphatic and saturated structures can facilitate the formation of functional groups (Figueiredo et al., 1999), consequently resulting in compounds with a more hydrophilic character, favoring the interaction with the soil. In addition, nitrogenous groups are formed due to the increase in the amount of N and to the lower C/N ratio.

Both the pH and PI of AH_{CH} were similar to those of the functionalized charcoals, indicating that the separation of the alkaline soluble material did not contribute to a specific modification of these potentiometric characteristics. The differences observed for the pH in water and the isoelectric point between CH and both CHox and AH_{CH} indicate modifications the carbonaceous surface due to functionalization with HNO_3. The low pH values are due to the functional groups formed and their intense protonation. While the PI of CH is greater than its pH, the PI of CHox and AH_{CH} are lower than their respective pH, which suggests the formation of functional groups with low dissociation potential, acting as weak acids. The low isoelectric point is interesting because the dissociation of functional groups will occur at low pH values, contributing to acidification and cation retention.

The potential cation exchange capacity (CEC) values of AH_{CH} and CHox were similar to those observed by Paiva et al. (2012) and Guimarães et al. (2015), being 4,400 and 4,750 $mmol_c\ kg^{-1}$, respectively. This result can be attributed to the functionalization of the charcoal.

From the XPS spectra, the highest intensity peaks were identified in relation to the characteristic energies of the chemical bonds in which C, O, and N participate. However, as the energy range for the identification of phenolic groups or ether is the same, it is not possible to conclude with precision the formation of one or the other, especially considering that some of the CHox and the AH_{CH} presented a proportion close to that of CH. As the ether functional group is common in the structure of CH, and considering that the potentiometric evaluations indicated an increase in the amount of phenolic groups, this supports the hypothesis that parts of the structure formed by ether have been converted into phenolic groups. Moreover, the lower proportion of aromatic and aliphatic C chains in CH, as opposed to the higher amount of carboxyl groups in CHox and AH_{CH}, suggests the predominance of the transformation of parts of the carbon structure into carboxyl groups.

The XPS spectrum contributes to enhancing the evidence of functional groups in the structure of the compounds. Certainly, these observations relate to the nitro compounds characterized by the NO_2-bond in both aliphatic and aromatic structures. As no type of N-containing bond was identified in CH, the insertion of N in CHox and AH_{CH} is evident.

The adsorption of the NH_3 by functionalized charcoal strongly suggests that both obtaining AH-like compounds from CH and functionalization with HNO_3 lead to the improvement of the adsorbent properties of charcoal. Considering that the evaluation was done in a media with a high NH_3 concentration, adsorption may have occurred by two processes: the occlusion of NH_3 in the pores of the compounds or protonation of NH_3, forming an NH_4^+ ion, followed by its adsorption by functional groups. The computed adsorption must be predominantly attributed to this process since during the drying of the sample, it is possible that the NH_3 in the pores has been removed. Kaneko et al. (1992) also attributed the high NH_3 adsorption by charcoal to the functional groups generated by its functionalization. High adsorption capacity is important because this would be one of the main factors involved in the reduction of N losses by NH_3 volatilization from urea mixed with functionalized charcoal. Thus, this characteristic is extremely important for this purpose.

The results of dry matter yield indicated that the interaction of urea with the functionalized charcoal potentiated corn growth. In addition, a lower N dose was required to obtain the same corn dry matter yield when urea was applied as U-CHox and U-AH_{CH} in contrast to applying urea alone. According to Guimarães et al. (2016), the high CEC of functionalized charcoal increases the availability of mineral N in the soil due to reducing N losses.

The treatments U-CHox6 and U-CHox9 showed an improved N-supply efficiency compared to the use of pure urea, at lower doses. The reduction in apparent N recovery efficiency for urea at higher doses is more probable because, in addition to reducing the efficiency of dry matter yield, a more saturated NH_3 environment is created, favoring its loss into the atmosphere. These latter results have also been observed by Primavesi et al. (2004), who found a smaller apparent N recovery by coastcross grass for higher doses of urea applied to the soil. The higher linear coefficient observed for U-CHox6 suggests a lower efficiency of this source compared to U-CHox9, indicating that the use of CHox, produced from functionalized charcoal with HNO_3, at a higher concentration does not provide a higher efficiency in the supply of N. The apparent N recovery efficiency of U-AH_{CH} was lower than that of pure urea; in the same way, the dry matter and N accumulation of corn plants fertilized with this source were lower than those observed for U-CHox6 and U-CHox9. However, Guimarães et al. (2015) found that compounds with physical-chemical properties similar to those of AH_{CH} were effective in reducing N losses of urea. As discussed above, the mode of incorporation of the compound into urea may have contributed to this result.

CONCLUSIONS

In summary, the physical and chemical properties of CHox are not influenced by the reaction time, but by the HNO_3 concentration. Moreover, the HNO_3 concentration also affects the capacity of CHox to adsorb NH_3. Adsorption of NH_3 by functionalized charcoal showed a positive correlation with the quantity of carboxylic and phenolic groups and a negative correlation with the pH value and the isoelectric point. These results lead us to infer that there is potential for the CHox or AH_{CH} compounds to improve the agronomic efficiency of urea. However, further studies are necessary to determine the most suitable dose to compose the urea-based fertilizer and the optimum N dose.

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AUTHOR CONTRIBUTIONS

Conceptualization: Diogo Mendes de Paiva and Reinaldo Bertola Cantarutti.

Investigation: Diogo Mendes de Paiva, Gelton Geraldo Fernandes Guimarães, and Breno Cardoso Teixeira.

Formal analysis: Diogo Mendes de Paiva and Gelton Geraldo Fernandes Guimarães.

Methodology: Diogo Mendes de Paiva and Reinaldo Bertola Cantarutti.

Software: Diogo Mendes de Paiva.

Writing – original draft preparation: Diogo Mendes de Paiva and Gelton Geraldo Fernandes Guimarães.

Writing – review and editing: Diogo Mendes de Paiva and Gelton Geraldo Fernandes Guimarães.

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