

Volatilization of Ammonia Originating from Urea Treated with Oxidized Charcoal

Gelton G. F. Guimarães,^a Diogo M. Paiva,^c Reinaldo B. Cantarutti,^{*a}
Edson M. Mattiello^a and Efraim L. Reis^b

^aDepartamento de Solos and ^bDepartamento de Química, Universidade Federal de Viçosa,
36570-900 Viçosa-MG, Brazil

^cCompanhia de Fertilizantes Galvani, 47850-000 Luiz Eduardo Magalhães-BA, Brazil

Loss of N through volatilization of ammonia is the main limitation for agricultural use of urea. The aim of this study was to evaluate the volatilization of NH₃ from urea granulated (Ug) or urea coated (Ur) with two oxidized charcoals produced by the oxidation of eucalyptus charcoal with 4.0 mol L⁻¹ HNO₃, followed by the post-treatment with NaOH (CHox) or without post-treatment with NaOH (CHox-OH). Ug and Ur were produced with 5, 10, 15 and 20% (m/m) of CHox or CHox-OH. The volatilization of NH₃ was evaluated as 100 mg of N in the form of Ug or Ur applied to samples of a Hapludalf placed in a system with continuous and controlled air flow. The Ug with CHox-OH or with CHox was more effective in reducing the volatilization of NH₃ than the Ur. It was estimated that the Ug with 16% of CHox or CHox-OH, with 39% N, reduced the volatilization by 40% in relation to urea without the additives. Results show that charcoal oxidized is an effective additive for reducing ammonia volatilization of urea.

Keywords: biochar, nitrogen, humic acids, humic substances

Introduction

The application rate and the mode of application of urea are determinants for the volatilization potential of NH₃.^{1,2} Surface application, common for topdressing fertilization, may lead to volatilization of up to 54% of the N applied.³ It is known that the volatilization of NH₃ from urea is less intense in soils with high acid buffering capacity and high cation exchange capacity (CEC), through favoring the formation and adsorption of NH₄⁺.^{4,5} In this context, evaluation was made with the mixture of urea with products with high CEC, such as zeolites with CEC of up to 1,200 mmol_c kg⁻¹ and humic acids (HA) with 5,200 and 8,327 mmol_c kg⁻¹.⁶⁻⁸ The carboxyl and phenolic groups are the most abundant ionizable sites in the HA, and they determine the acid character, the high acid buffering capacity and high CEC.⁹ Yusuff *et al.*⁷ verified that the application of 2.02 g of urea combined with 0.75 or with 1.00 g of HA extracted from soil (5,200 mmol_c kg⁻¹), or with 0.75 g of HA plus 0.75 g of fine air-dried earth of a tiomorphic soil (405 mmol_c dm³ of CEC and pH 3.45) reduced the volatilization of NH₃ by 31, 36 and 33%,

respectively. Rosliza *et al.*⁸ found that the addition of 0.75 g of HA (8,327 mmol_c kg⁻¹) or 60 mL kg⁻¹ of fulvic acids (FA) to the mixture of sand, triple superphosphate and potassium chloride reduced the volatilization of NH₃ by 13 and 30%, respectively. In spite of these evident reductions in volatilization, it should be considered that the extraction of HA from the soil or from peat leads to greater environmental impacts because of the mining process these raw materials.

Substances equivalent to the HA and FA may be produced by oxidation of charcoal with HNO₃,^{10,11,12} with the advantage of using a renewable source of C. Using this procedure, Paiva *et al.*¹³ obtained substances equivalent to HA with 4,400 mmol_c kg⁻¹ of CEC, denominated oxidized charcoal (CHox). These authors verified that the prilled urea coated with 25% (m/m) of CHox in the laboratory reduced the volatilization of NH₃ by up to 42% and delayed the peak of maximum volatilization by 24 h. These effects were attributed to the high acidity potential of the CHox; however, these authors argue that a greater contact of the CHox with the urea would provide for a more effective control of the volatilization of NH₃. Paiva *et al.*¹³ emphasize that the solubilization in alkali or acid for extraction of HA and FA increases salinity and, consequently, dialysis time, in addition to bringing about the loss of the precipitated

*e-mail: cantarutti@ufv.br

fraction and soluble fraction in alkali, which are equivalent to the humins (HU) and FA, respectively. Therefore, the yield of CHox production is reduced and fractions with high electrochemical potential are lost. In suppressing the alkali treatment, they argue that the CHox would contain a mixture of substances equivalent to HA, FA and HU. Thus, in this paper, the oxidized coal produced without alkali treatment (CHox-OH) was characterized and the NH₃ volatilization from urea granulated obtained from the treatment was evaluated.

Experimental

Production and oxidation of charcoal

Charcoal (CH) was produced from *Eucalyptus urophylla* wood carbonized at 350 °C for 8 h in a laboratory oven and it was then grounded to a texture of less than 74 µm and dried at 105 °C for 12 h.

The CH was oxidized with 4.0 mol L⁻¹ HNO₃ at the proportion of 45 g L⁻¹, keeping the mixture heated to boiling under reflux for 4 h. After 12 h of rest at ambient temperature, the mixture was filtered, obtaining a residue. For the production of oxidized charcoal (CHox), this residue was dissolved in a 0.5 mol L⁻¹ NaOH solution and, after 12 h rest, the mixture was centrifuged (1.834 g for 30 min). The residue insoluble in alkali was discarded, and the supernatant was acidified at pH 2.0 with 5.7 mol L⁻¹ H₂SO₄ and kept at ambient temperature for 12 h. After that, it was centrifuged and the supernatant discarded, while the residue insoluble in acid was solubilized in 0.5 mol L⁻¹ NaOH and then once more acidified at pH 2.0. After 12 h of rest, it was centrifuged and the residue insoluble in acid (CHox) was subjected to dialysis in membrane tubes (Sigma Dialysis Tubing 23 mm MWCO12400 retention of 99.9%) immersed in distilled water. The water was exchanged twice a day until there was no increase in its electrical conductivity greater than 2 µS one hour after the exchange. After that, the CHox was dried at 40 °C in a laboratory oven and grounded to a texture less than 74 µm.

For production of oxidized charcoal without the treatment with NaOH (CHox-OH), the residue from oxidation in acid, retained in the first filtering, was dissolved in deionized water and subjected to dialysis, as already described. After dialysis, the CHox-OH was dried and grounded in the same manner as the CHox.

Characterization of the CHox and the CHox-OH

The C, H and N contents were determined in an elemental analyzer (Perkin-Elmer 2400 Series II CHNS/O

Analyser) and were expressed in relation to dry matter free of ash. The oxygen content was estimated by the difference between the matter free of ash and the C, H and N contents; and the C/N, H/C and O/C atomic ratios were calculated.

The pH in the suspension of 1.0 g of CHox or CHox-OH in 10 mL of deionized water was determined. The contents of the carboxyl and phenolic functional groups were determined by potentiometric titration, after initial acidification of the samples to pH ca. 2.0 according to Paiva *et al.*¹³ and Reis *et al.*¹⁴ The pK_a values of the functional groups were estimated by means of multiparametric regression, which describes the potentiometric titration of a mixture of a strong acid with *n* weak acids with a strong base.¹⁴ Total acidity was defined by the total of the carboxyl functional groups from pH 3.0 to 8.0 and phenolic functional groups from pH 8.0 to 10.0, according to Inbar *et al.*¹⁵

The samples were analyzed by Fourier transform infrared (FTIR) spectroscopy using the GradiATR accessory, which allows readings of attenuated total reflectance (ATR) in the spectral band of 4,000 to 400 cm⁻¹, with resolution of 4 cm⁻¹.

Urea granulated with CHox or with CHox-OH and prilled urea coated with CHox or CHox-OH

The analytical grade urea (46% N) was melted in a vessel immersed in glycerin heated to 137 °C, and homogenized with 5, 10, 15 or 20% (m/m) of CHox or CHox-OH. The granulated urea (Ug) was produced by dripping the molten mixture over a steel plate using an automatic pipette. With the immediate cooling, granules were formed in the shape of drops with a diameter from 4 to 5 mm and height from 2 to 3 mm. The urea without oxidized charcoal was also granulated.

To obtain the coated urea (Ur), the commercial prill urea (45% N) were mixed with 5, 10, 15 or 20% CHox or CHox-OH, with the addition of vegetable oil to promote adhesion. The mixing was performed in glass tubes by gently shaking to allow homogenous coating. By the difference between the initial and final weight of the urea, after coating, it was observed that coating of 4.7, 10.5, 14.6 and 19.8% of CHox or CHox-OH had occurred.

To determine the N content, 1 g of Ug and Ur with CHox or CHox-OH, 0.7 g of Raney alloy, 5 mL of concentrated H₂SO₄ and 10 mL of distilled water were heated to 250 °C in a digester block until complete oxidation of the sample and the N was dosed by Kjeldahl distillation. In the Ug-CHox, 440, 420, 390 and 370 g kg⁻¹ of N were obtained, and in Ug-CHox-OH, 430, 420, 390 and 380 g kg⁻¹ were obtained, according to the increase in the proportions of the respective

oxidized charcoals. In the Ur with CHox, these contents were 410, 390, 370 and 350 g kg⁻¹, and with CHox-OH, they were 410, 400, 390 and 350 g kg⁻¹.

Volatilization of ammonia from urea granulated or prilled urea coated with CHox or CHox-OH

The volatilization of NH₃ in the laboratory was evaluated using an air-dried sample from an Hapludalf with texture less than 2 mm with 500 g kg⁻¹ of clay; pH (H₂O) of 6.8; 38.6 mg dm⁻³ of P and 168 mg dm⁻³ of K extracted by Mehlich-1; 5.4 and 1.96 cmol_c dm⁻³ of Ca^{II} plus Mg^{II}, respectively, extracted by 1 mol L⁻¹ KCl; 1.70 cmol_c dm⁻³ of potential acidity (H+Al), extracted by CH₃COOCa pH 7.0; 9.49 of cation exchange capacity (CEC) at pH 7.0; 82% of base saturation; and 46 g kg⁻¹ of organic matter (Walkley-Black).

The experiment was conducted in a system composed of incubation chambers (glass container of 340 cm³) connected to ammonia capture units (erlenmeyer flasks with 40 mL of a 20 g L⁻¹ H₃BO₃ solution). The system received a continuous flow of air of approximately 300 cm³ min⁻¹, free of NH₃ and moistened to promote renewal of the atmosphere in the chambers and the drawing of NH₃. Three day before the beginning of the trial, 100 cm³ of the soil was placed in incubation chambers and the soil moisture was raised to 80% of the moisture equivalent with distilled water and was maintained at 25 ± 2 °C. The quantities of Ug or Ur with the different proportions of CHox or CHox-OH sufficient for supplying 100 mg of N were applied on the soil and lightly compressed. The chambers were immediately sealed, initiating the air flow. Evaluations occurred in 12, 24, 48, 72, 96, 120, 144 and 168 h after the beginning of the flow, removing the capture units, which were replaced by others at the end of each period of time. The NH₃ collected was quantified by potentiometric titration of the H₃BO₃ to pH 4.6 with 80 mmol L⁻¹ HCl. Soil moisture was monitored by weight variation of the incubation chambers and, when necessary, distilled water was injected through a lateral orifice, sealed with rubber.

Thus, the treatments resulted from the factorial combination (2 × 2 × 4) + 3, which correspond to the two oxidized charcoals (CHox or CHox-OH), the two forms of urea (granulated or coated prilled), and the four proportions of the oxidized charcoals (5, 10, 15 or 20%). The three additional treatments were performed: the granulated urea and the prilled urea without oxidized charcoal and the soil without application of urea. The experimental design was randomized blocks with four replications.

The quantity of volatilized NH₃, excluding the quantity volatilized from the soil without the application of urea, was

expressed in relation to the quantity of N applied (mg g⁻¹ of N-NH₃) and as the volatilization rate (VR) (mg g⁻¹ h⁻¹ of N-NH₃). The results were subjected to analysis of variance (VR). The VR (y) was related to evaluation time (x) by regression equations according to the non-linear model denominated the vapor pressure model:

$$y = e^{\left(a + \frac{b}{x} + c \ln(x)\right)} \quad (1)$$

The first derivative of this equation is:

$$\frac{dy}{dx}(x) = \left(-\frac{b}{x^2} + \frac{c}{x}\right) e^{\left(a + \frac{b}{x} + c \ln(x)\right)} \quad (2)$$

equaled to zero, results in $x = b/c$, in which "x" is the time in which the maximum rate of volatilization (t_{mx}) occurred, as of which the VR_{mx} was estimated. The VR at 72 h (VR₇₂) and 96 h (VR₉₆) from application of the urea were also estimated. The total quantity of ammonia volatilized was related to the proportions of oxidized charcoal by regressions, which were compared by the identity test of linear models ($p < 0.10$).^{16,17}

Results and Discussion

Production and characterization of CHox and CHox-OH

The yield of CHox and of CHox-OH in relation to the initial weight of charcoal (CH) was 327 and 784 g kg⁻¹, respectively. Oxidation of CH reduced the carbon contents in the CHox and CHox-OH by 28 and 21%, respectively. There were no appreciable changes in hydrogen contents; nevertheless, the N contents increased around three times. There were also increases of 1.8 and 1.6 times in the oxygen contents in CHox and CHox-OH, respectively. The C/N ratios of CHox and CHox-OH did not differ, but were around 4.4 times less than the C/N of the CH. Oxidation of the CH did not change in an expressive way the H/C ratio; however, it more than doubled the O/C ratio (Table 1).

The two forms of oxidized CH were extremely more acidic than the CH (Table 1). Total acidity of the CHox, which characterizes the CEC potential, was greater than that of the CHox-OH, and they were 9.7 and 8.4 times greater than the total acidity of the CH, respectively. The carboxyl functional groups were responsible for 78 and 76% of the total acidity in the CHox and in the CHox-OH, respectively (Table 1).

The potentiometric titration curves exhibit the greater acid buffering capacity of the CHox and CHox-OH (Figure 1) but, visually, they indicate only a point of inflection.

Five partial volumes of equivalence in titration were identified when the point to point with the second derivative of the titration curve is null, which define non-perceptible points of inflections. As of these volumes, by multiparametric non-linear regression that describes the titration,¹⁴ five values of pK_a from 1.2 to 9.6 were estimated, without large discrepancies between the CHox and the CHox-OH (Table 2).

Table 1. Chemical characteristics of eucalyptus charcoal (CH) and of oxidized CH, with (CHox) or without (CHox-OH) alkali treatment

Characteristic	CH	CHox	CHox-OH
C / (g kg ⁻¹) ^a	735	533	581
H / (g kg ⁻¹) ^a	34	31	32
N / (g kg ⁻¹) ^a	9	28	33
O / (g kg ⁻¹) ^a	222	408	355
C/N	97	22	21
H/C	0.56	0.70	0.65
O/C	0.40	1.02	0.82
pH (H ₂ O) ^b	6.8	2.8	2.7
Carboxyl groups / (mmol _c kg ⁻¹) ^c	300	3,780	3,180
Phenolic groups / (mmol _c kg ⁻¹) ^c	200	1,070	980
Total acidity / (mmol _c kg ⁻¹) ^d	500	4,850	4,170

^aIn relation to dry matter free of ash; ^bcharcoal: water ratio of 1:10; ^cestimated by potentiometric titration; ^dsum of the carboxyl groups (pH 3.0-8.0) and phenolic groups (pH 8.0-10.0).

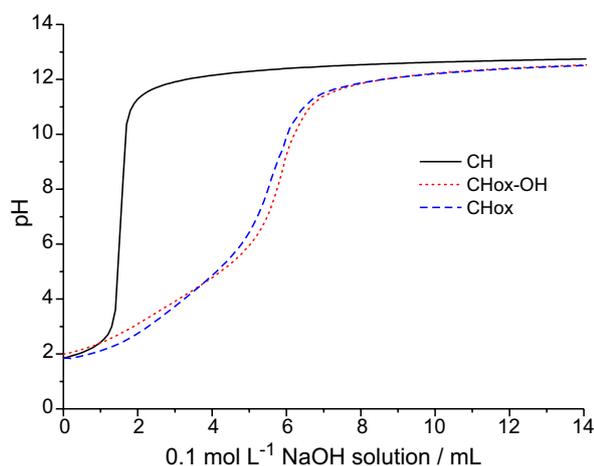


Figure 1. Potentiometric titration curve, from materials with initial pH adjusted to 2.0, characterized by the variation of the pH of the suspensions of the eucalyptus charcoal (CH) and of the oxidized CH without alkali treatment (CHox-OH) or with alkali treatment (CHox), according to the volume of the 0.1 mol L⁻¹ NaOH solution.

The CHox and CHox-OH infrared spectra were different from the CH spectra, but similar to each other, with characteristic peaks, varying in intensity but not in regard to absorption frequencies (Figure 2). They show well-defined peaks in the absorption bands characteristic

Table 2. Values of pK_a of the oxidized eucalyptus charcoal with alkali treatment (CHox) or without alkali treatment (CHox-OH), estimated by multiparametric non-linear regression, which describes the titration of the mixture of a strong acid with n weak acids titrated with a strong base

Charcoal	pK_{a1}	pK_{a2}	pK_{a3}	pK_{a4}	pK_{a5}
CHox	1.4	3.7	5.3	7.2	9.6
CHox-OH	1.2	3.6	5.3	7.3	9.4

of stretching of the C=O (carboxyl) (1,703 cm⁻¹ and 1,706 cm⁻¹) and N=O (nitro) (1,534 cm⁻¹ and 1,533 cm⁻¹) bonds. In these materials, the carboxyl functional group is predominant and is mainly responsible for high total acidity, which determines the acidic character and the high buffering capacity.

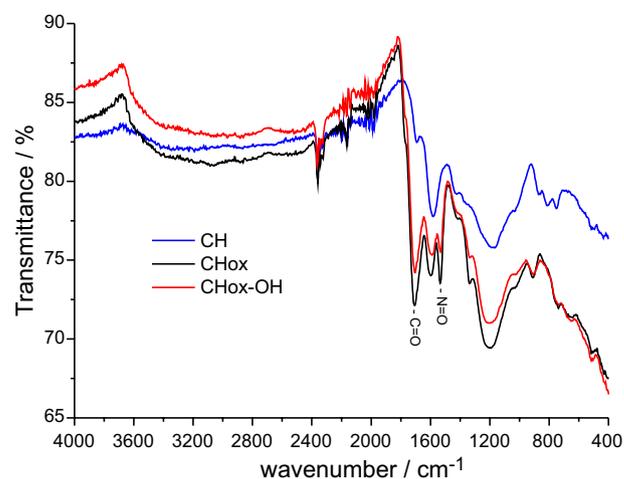


Figure 2. Infrared spectra of eucalyptus charcoal (CH) and of oxidized CH with alkali treatment (CHox) or without alkali treatment (CHox-OH).

Volatilization of ammonia from urea granulated or coated with CHox or CHox-OH

Variation in the volatilization rate of N-NH₃ over time, both for urea granulated and for urea coated with the different proportions of CHox or CHox-OH (Figure 3) fitted adequately to the Vapor Pressure Model (Table 3).

The granulated urea showed a volatilization peak of NH₃ (t_{mx}) 38 h after application. Although the volatilization rate at this time was the lowest, the accumulated volatilized quantity was the greatest (517.4 mg g⁻¹), which may be explained by the intense volatilization for more time, as shown by the rates at 72 (VR₇₂) and 96 h (VR₉₆) (Table 3). The commercial prilled urea exhibited a greater rate of volatilization in the t_{mx} of 38 h, but accumulated a lower quantity of volatilized N-NH₃ (468.8 mg g⁻¹) (Table 3).

The accumulated quantity of NH₃ volatilized in 168 h by urea granulated with CHox or CHox-OH ranged from 286.9 to 384.3 mg g⁻¹ (Table 3). The urea granulated with

5% CHox (UgCHox5) or CHox-OH (UgCHox-OH5) exhibited the greatest rates at the peak of volatilization, 6.07 and 5.94 mg g⁻¹ h⁻¹, respectively, in spite of the accumulated losses having been less than the granulated urea (Table 3). Considering that the peaks of volatilization occurred around 40 h after application, this is explained by the lower rates of volatilization at 72 and 96 h. The

UgCHox20 and UgCHox-OH15 exhibited t_{max} at 44 h after application, with lower rates, 3.6 and 3.8 mg g⁻¹ h⁻¹ of N-NH₃, respectively (Table 3). Nevertheless, the urea granulated with 15% CHox (UgCHox15), or with 10% CHox-OH (UgCHox-OH10) with maximum volatilization rates of 4.86 and 4.46 mg g⁻¹ h⁻¹, respectively, were those that led to the smallest quantities of volatilized NH₃, which

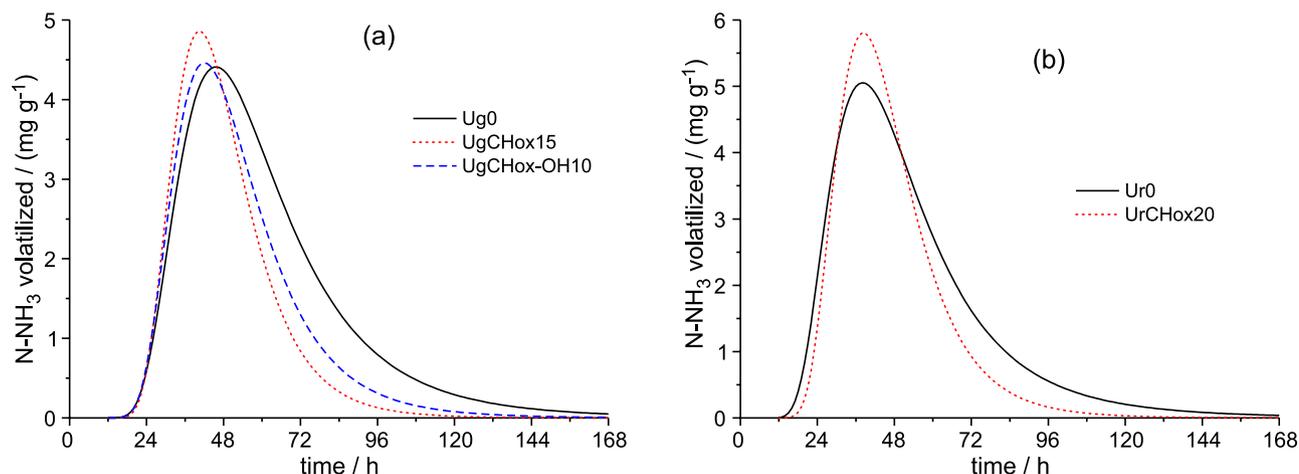


Figure 3. Rate of N-NH₃ volatilization of the urea granulated with 0, 10 and 15% of oxidized charcoal (CHox or CHox-OH) in (a) and of prilled urea coated with 0 and 20% of oxidized charcoal (CHox) in (b), from 12 to 168 h of application on the soil and maintained in a closed system with continuous air flow.

Table 3. Equation coefficients of the regression that relate the rate of NH₃ volatilization to the time since its application (12 h to 168 h) of granulated urea, prilled urea, urea granulated (Ug) or of prilled urea coated (Ur) with 5, 10, 15 and 20% CHox or CHox-OH, correlation between values observed and estimated by the regression equations (R²), maximum rate of volatilization (VR_{max}), time in which VR_{max} (t_{max}) occurred, volatilization rate in 72 h (VR₇₂) and 96 h (VR₉₆), volatilized N-NH₃ accumulated in 168 h (mg g⁻¹) and the percentage of reduction in volatilization (RV)

Urea	Coefficient ^a			R ² y	t _{max} / h	VR _{max} / (mg g ⁻¹ h ⁻¹)	VR ₇₂ / (mg g ⁻¹ h ⁻¹)	VR ₉₆ / (mg g ⁻¹ h ⁻¹)	N-NH ₃ / (mg g ⁻¹)	RV ^{(III)c} / %
	a	b	c							
U granulated (Ug)	39.12	-356.14	-7.81	0.93	46	4.41	2.18	0.80	517.4	-
U prilled (Ur)	33.63	-263.02	-6.90	0.93	38	5.05	1.62	0.55	468.8	-
Urea granulated with CHox or CHox-OH ^b										
UgCHox5	55.48	-459.28	-11.44	0.98	40	6.07	1.20	0.22	384.3	26
UgCHox10	55.59	-460.01	-11.49	0.98	40	5.55	1.08	0.20	347.8	33
UgCHox15	61.44	-515.74	-12.73	0.96	41	4.86	0.84	0.13	286.9	45
UgCHox20	46.00	-408.54	-9.37	0.96	44	3.60	1.32	0.37	327.0	37
UgCHox-OH5	52.58	-427.36	-10.87	0.98	39	5.94	1.15	0.22	373.8	28
UgCHox-OH10	49.38	-424.62	-10.11	0.98	42	4.46	1.30	0.31	349.3	33
UgCHox-OH15	44.51	-398.02	-9.02	0.96	44	3.81	1.51	0.45	366.9	29
UgCHox-OH20	45.95	-386.51	-9.42	0.97	41	4.64	1.33	0.34	366.9	29
Prilled urea coated with CHox or CHox-OH ^b										
UrCHox5	60.34	-479.31	-12.54	0.95	38	8.29	1.06	0.15	429.7	8
UrCHox10	46.12	-375.38	-9.47	0.96	40	6.04	1.50	0.36	440.9	6
UrCHox15	43.66	-349.15	-9.00	0.95	39	5.74	1.40	0.35	421.0	10
UrCHox20	54.09	-431.77	-11.26	0.91	38	5.81	0.93	0.16	334.5	29
UrCHox-OH5	40.62	-329.57	-8.33	0.95	40	5.19	1.51	0.43	427.3	9
UrCHox-OH10	50.68	-389.87	-10.55	0.97	37	7.80	1.17	0.22	441.2	6
UrCHox-OH15	44.88	-365.94	-9.22	0.97	40	5.51	1.42	0.36	413.5	12
UrCHox-OH20	52.11	-414.33	-10.79	0.95	38	7.06	1.23	0.23	425.1	9

^aCalculated based in the equation (1): $\hat{y} = e^{\left(a + \frac{b}{x} + c \ln(x)\right)}$; ^bCHox and CHox-OH: oxidized charcoal produced from *Eucalyptus* charcoal with and without alkali treatment after oxidation with HNO₃, respectively; ^creduction percentages is due to Ug or Ur with the different proportions of oxidized charcoal in relation to granulated and prilled urea, respectively.

corresponded to reductions of 45 and 33% in volatilization in relation to granulated urea (Table 3).

With the prilled urea coated with the oxidized charcoals (Ur), the total quantities of volatilized N-NH₃ range from 334.5 to 467.9 mg g⁻¹ and the t_{mx} from 37 to 40 h after application (Table 3). The urea coated with 5% CHox led to the greatest volatilization rate and, therefore, the greatest total quantity of N-NH₃ lost (429.7 mg g⁻¹). At the level of 20%, the greatest reduction in volatilization of the prilled urea coated with CHox (29%) was achieved (Table 3). For the coating with CHox-OH, however, the lowest rate (5.51 mg g⁻¹ h⁻¹) and the lowest total volatilized quantity (413 mg g⁻¹) occurred at the level of 15%, but corresponded to reduction of only 12% in relation to prilled urea (Table 3).

Granulation of urea with the growing proportions of CHox or CHox-OH led to statistically equivalent reductions in the quantities of volatilized N-NH₃, according to the model identity test (Figure 4). Based on this equation, it is estimated that the urea granulated with 16% CHox or CHox-OH leads to the greatest reduction in volatilization. In contrast, only the prilled urea coating with CHox led to significant reduction in the volatilization of NH₃ (Figure 4), but the greatest reduction was achieved with the addition of 20% CHox (UrCHox20).

The yield of CHox in relation to the initial mass of CH was greater than the yields obtained by Trompowsky *et al.*¹¹ and Paiva *et al.*¹³ The greater yield in production of CHox-OH is due to aintenance of the fraction insoluble in alkali,¹⁸ which is discarded in the first treatment with NaOH in production of CHox and which is certainly composed with characteristics similar to the humin.¹³ In the process of separation of the CHox, there are also soluble compounds discarded in the alkali and acid extracts, which would be compounds equivalent to the FA, which was shown by the tan coloring of the extracts. Although the quantity is not sufficient to compromise the yields of the CHox, a fraction with high electrochemical potential for generation of negative electrical charges is lost.

The C content in the oxidized charcoals were less than those reported in a similar process of oxidation of charcoal.^{11,13} Although the C/N ratios were near those found by these authors, the O/C ratio was twice as large in the present CHox. The increases of the N and O contents in CHox and CHox-OH are due to the incorporation of functional groups like N=O, present in the nitrobenzene structure, and of functional groups containing O, like carboxyls and phenolics.¹¹ The predominance of the carboxyl groups in HA extracted from soil and vermicompost is also reported.^{7,8,9} The lower total acidity of the CHox-OH is due to the dilution with the inclusion of the fraction insoluble in alkali, which are like the HU,

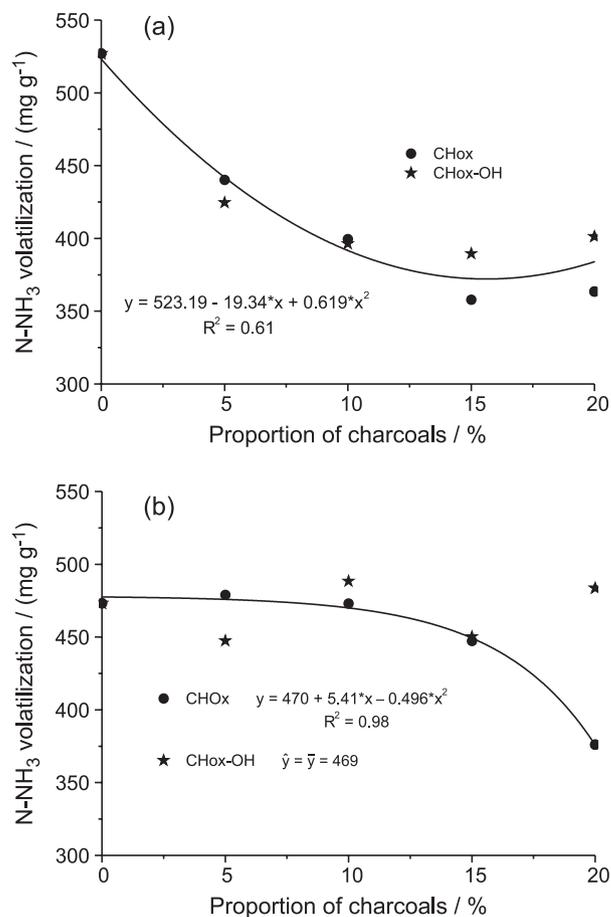


Figure 4. Quantity of N-NH₃ volatilized according to the proportion of CHox or CHox-OH in granulated urea in (a) or in coated prilled urea in (b) 168 h after application on the soil in a closed system with continuous air flow. For granulated urea, the regression equation characterizes the mean trend for CHox and CHox-OH. ** and ° significant at 1 and 10%, respectively.

and which are recognized to have total acidity less than the HA.^{19,20}

The broad range of variation of the pK_a of the CHox and CHox-OH is related to the variation in the chemical characteristics of the ionizable functional groups, such as the carboxyls, phenolics and nitro, or groups of the same nature, however with different intermolecular interactions.¹⁴ The pK_a values of the CHox and CHox-OH (3.6 to 9.6) are in agreement with the pK_a of carboxyl groups (5.5 and 6.0) and phenolic groups (9.0 and 9.8) of humic substances and humic acids.^{9,14,21,22} The lowest values of pK_a of CHox (1.4) and of CHox-OH (1.2) were less than the lowest pK_a for HA (2,8 e 3,4)^{9,14} and are equivalent to the pK_a of strong acids. Thus the pK_{a2} (3.6 and 3.7) and the pK_{a3} (5.3) of the CHox and CHox-OH are attributed to the carboxyl groups, and the pK_{a4} (7.2 and 7.3) and pK_{a5} (9.4 and 9.6) to the phenolic groups.^{9,21} With such characteristics, both the CHox and the CHox-OH have potential to alleviate the rise of pH arising from hydrolysis of the urea, which may reach 8.7.²³

The absorption bands of the CHox and CHox-OH are compatible with the absorption bands from 1,715 cm^{-1} to 1,690 cm^{-1} attributed to the α,β -unsaturated aliphatic carboxyl functional groups.²⁴ The presence of the 1,534 cm^{-1} and 1,533 cm^{-1} peaks characterize the deformation attributed to N=O bonds in nitrobenzene.^{24,25} These functional groups were also identified in substances equivalent to humic acids obtained from charcoal by a similar process.¹¹ The absence of these characteristic bands in the spectrum of the CH indicates that these functional groups arose from its oxidation.

The lower volatilization achieved from the prilled urea may be attributed to the greater hardening of the granule due to the formaldehyde added during formation of the prills, which conditions lower solubility than granulated urea produced from urea p.a. In spite of that, the greater reduction in volatilization of NH_3 , of 29%, obtained by coating the urea with 20% CHox, was less than the 45% observed by Paiva *et al.*¹³, although these authors worked with the addition of 25% oxidized charcoal. It should be noted that the need for a greater proportion of CHox implies a lower N content in the coated urea. It was observed that the oxidized charcoals that coated the prilled urea dissolved and is concentrated on the soil surface near the prills, which restricted contact with the urea that spread in the soil mass. This fact may explain the lower effectiveness than that achieved by Paiva *et al.*¹³

The more effective reduction of volatilization of NH_3 with urea granulated with CHox or CHox-OH shows the importance of greater contact of the oxidized charcoals with the urea. It was observed that the granulated urea, both with the CHox and the CHox-OH, dissolved and spread into the soil mass, which contributed to greater contact with the urea and to the effectiveness of both in reduction of volatilization of NH_3 . Although the CHox-OH has 14% less total acidity, it is still very high, and its chemical similarity to the CHox may be characterized by the values and by the amplitude of variation of the pK_a . Values of pK_a as high as 7.2 and 9.6 allow the dissociation of H from functional groups in high pH, like that which occurs in hydrolysis of urea. As well as favoring the formation of NH_4^+ , charges are created for its adsorption. Reduction of 35% in volatilization of NH_3 was observed with the mixture of urea with 370 mg g^{-1} of HA.⁷ In recent literature,²⁶ there is the indication that carbonaceous products like "biochar" contribute to NH_3 retention in the soil. The "biochar" produced from wood (*Pinus radiata*) shavings with pyrolysis from 300 to 500 °C, for example, with characteristics similar to those of the oxidized charcoals and of HA, incorporated in the soil, significantly reduced the volatilization of NH_3 originating from the urine of ruminants and increased N availability.

"Biochar", produced from corn husk, increased total N retention in the surface layer of the soil, although it did not cause an increase in corn production.²⁷ The acidic nature and the high CEC of the HA are responsible for reduction of volatilization of NH_3 and for the increase of exchangeable NH_4^+ in the soil.⁸ The effect of "biochar" on the N stock and N dynamic in the soil is achieved with rates as high as 30 t ha^{-1} , nevertheless, information in respect to its use associated with nitrogen fertilizers is still limited.²⁷ The proportion of only 16% of CHox or CHox-OH of the aggregate to the granule leads to urea with 39% N and conditions reduction in the order of 40% in volatilization of NH_3 in relation to urea without the additive.

Conclusions

Summing up, it may be concluded that the suppression of the alkali treatment increases the yield in production of oxidized charcoal. It may likewise be concluded that this procedure produces an oxidized charcoal (CHox-OH) with structural and physicochemical characteristics similar to those of the oxidized charcoal treated with alkali (CHox). The urea granulated with CHox-OH or CHox is more effective in reduction of volatilization of NH_3 than the coated prilled urea. The urea granulated with 16% CHox-OH or CHox has 39% N and leads to a 40% reduction in volatilization of NH_3 .

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