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Sequential Ammonia and Carbon Dioxide Adsorption on Pyrolyzed **Biomass to Recover Waste Stream Nutrients**

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ABSTRACT: The amine-rich surfaces of pyrolyzed human solid waste (py-HSW) can be "primed" or "regenerated" with carbon dioxide (CO_2) to enhance their adsorption of ammonia (NH_3) for use as a soil amendment. To better understand the mechanism by which CO_2 exposure facilitates NH_3 adsorption to py-HSW, we artificially enriched a model sorbent, pyrolyzed, oxidized wood (py-ox wood) with amine functional groups through exposure to NH₃. We then exposed these N-enriched materials to CO_2 and then resorbed NH_3 . The high heat of CO₂ adsorption (Q_{st}) on py-HSW, 49 kJ mol⁻¹, at low surface

• NH₃ 🌉 Weight change CO₂ purge

Time the high field of OO_2 and OO_2 a adsorption is favorable for CO₂ uptake. Adsorption kinetics of py-ox wood revealed continued, albeit diminishing NH₃ uptake after each CO_2 treatment, averaging 5.9 mmol NH₃ g⁻¹ for the first NH₃ exposure event and 3.5 and 2.9 mmol NH₃ g⁻¹ for the second and third; the electrophilic character of CO2 serves as a Lewis acid, enhancing surface affinity for NH3 uptake. Furthermore, penetration of ¹⁵NH₃ and ¹³CO₂ measured by NanoSIMS reached over 7 µm deep into both materials, explaining the large NH₃ capture. We expected similar NH₃ uptake in py-HSW sorbed with CO₂ and py-ox wood because both materials, py-HSW and py-ox wood sorbed with NH₃, had similar N contents and similarly high CO₂ uptake. Yet NH₃ sorption in py-HSW was unexpectedly low, apparently from potassium (K) bicarbonate precipitation, reducing interactions between NH₃ and sorbed CO₂; 2-fold greater surface K in py-HSW was detected after exposure to CO₂ and NH₃ than before gas exposure. We show that amine-rich pyrolyzed waste materials have high CO2 affinity, which facilitates NH3 uptake. However, high ash contents as found in py-HSW hinder this mechanism.

KEYWORDS: pyrolysis, biochar, human solid waste, nitrogen, ammonia, carbon dioxide, adsorption

INTRODUCTION

In communities lacking sewerage, indiscriminate disposal of nutrient-enriched liquids and pathogen-laden solid wastes poses environmental and sanitation hazards.^{1,2} At the same time, between 70 and 90% of waste nitrogen (N) is excreted in the urine in the form of urea (CH₄N₂O), a commonly applied N fertilizer worldwide.³⁻⁵ Technologies for N removal from wastewater can help reduce environmental contamination while promoting recovery of fertilizer nutrients as soil amendments.^{6,7}

Zeolites, ion-exchange resins, and activated carbon have been investigated to trap plant-available N species such as ammonium (NH_4^+) and nitrate (NO_3^-) from liquid streams. $^{8-15}$ Ammonia gas (NH_3) is another concern due to its high toxicity, with point-source pollution arising from fertilizer,^{16,17} animal production,¹⁸ and composting.¹⁹ Ammonia capture on solid sorbents occurs through hydrogen bonding²⁰ and acid-base reactions, as NH₃ functions both as a proton-accepting Bronsted base and as an electron-donating Lewis base. 17,21,22 In the presence of water, NH₃ adsorbs to solid sorbents electrostatically as NH4⁺.^{8,178,17} In

dry systems, NH₃ adsorption occurs through nucleophilic addition via interaction of the lone electron pair on NH₃-N and an electrophilic C on the sorbent scaffold.²¹ Hydrogen bonding between NH₃ and oxygenated functional groups is another mechanism for NH₃ adsorption.²⁰ For this reason, oxidized carbonaceous substrates such as graphene oxide are excellent $\rm NH_3$ sorbents. 17,23,34

Dry scrubbing of NH3 has proven effective with oxidized graphene and activated carbon.²⁰⁻²⁴ Another option for sorbents, which combines the high adsorption potential of zeolites or activated carbon, is pyrolyzed biomass or biochar.²⁵ Pyrolysis may convert straw, woody shrubs, and manure solids into porous, surface-functionalized adsorbents.⁸ As most biomass feedstocks are waste materials, they can be locally

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available and do not require regeneration such as zeolites or activated carbon but can be applied as soil amendments.²⁵

The NH₃ retention capacity of pyrolyzed materials may vary with the physical and chemical characteristics of the original material. Pyrolyzed plant biomass or biochar contains carboxylic functional groups, which can adsorb NH₃.^{8,25} In one study, the total N content of pyrolyzed wood oxidized with hydrogen peroxide (H₂O₂) increased by 9% (w w⁻¹) after exposure to NH₃ gas through both physisorption and chemisorption.²⁶ In another study, the total N content of a low-temperature woody biochar mixed in soil increased by 0.6% (w w⁻¹) through sorption of ¹⁵NH₃ volatilizing from cow urine. Sorbed ¹⁵NH₃ was both KCl extractable and plant available to ryegrass.²⁵

Unlike most plant feedstocks used for biochar production, manures including human solid waste are high in organic N and mineral ash, which may affect the sorption dynamics of NH₃. Fecal sludge biochar was shown to be an effective NH₄⁺ sorbent, removing over 18 g N g⁻¹ from NH₄+Cl⁻ solution.²⁷ Moreover, poultry biochar sorbed slightly less NH₄⁺ compared to wood biochar from NH₄+NO₃⁻ solution,²⁸ 19.8 vs 26.3 mg N g⁻¹. However, the effectiveness of ash-rich manure biochars as NH₃ sorbents is unknown. As pyrolysis gains interest for waste management, biochar derived from human waste²⁷ may be useful for stripping volatile NH₃ from wastewater and urine.^{7,25} However, no study has investigated the creation of a N-rich fertilizer using human solid waste biochar as a sorbent for NH₃.

The structural changes in N compounds following pyrolysis^{29,30} may not enhance a material's ability to sorb NH₃ but may facilitate another type of interaction, CO₂ adsorption. Significantly greater N in 6-membered rings was detected in woody biomass with increasing pyrolysis temperature, from 300 to 700 °C. A clear correlation was also observed between N-heterocycles in pyrolyzed biomass and the initial feedstock N content.²⁹ The acid-hydrolyzable fraction of N in biosolids was observed to decrease from 83 to 5% after pyrolysis at 550 °C, with a shift toward aminosugar compounds instead of amino acids.³⁰ These Ncontaining surface functional groups, primary, secondary, and tertiary amines, have properties of Lewis and Bronsted bases that are not effective in trapping NH₃, but which are useful in chemisorbing CO_2 . Chemisorption of CO_2 onto primary amines under dry conditions generates carbamates through cooperative binding of two adjacent primary amines. Secondary amine uptake of CO2 forms carbamic acid and does not involve cooperative binding.^{31–35} Tertiary amines can only interact with CO_2 in the presence of water vapor to form bicarbonate.³⁵⁻³⁷ What has not been investigated is whether these products resulting from the CO₂ reaction with amine groups, such as carbamate, carbamic acid, and bicarbonate, are able to bond with NH₃.

For this study, we examined whether exposure to CO_2 enhances the affinity for NH_3 uptake in a sorbent inherently enriched with amine groups. We were interested in whether pyrolyzed human waste (py-HSW) characterized by surface basicity due to amine functional groups could sorb NH_3 following a single pre-exposure to CO_2 . To determine the robustness of surface repriming with CO_2 in facilitating NH_3 uptake without potentially confounding effects of ash minerals, we artificially enriched an ash-poor sorbent with amine functional groups through exposure to NH_3 and then evaluated whether repeated exposure to CO_2 facilitates additional NH_3

uptake. We chose a biomass-derived sorbent previously reported to have high NH_3 sorption capacity and low ash content, pyrolyzed oxidized wood (py-ox wood).²⁶

In using isotopically enriched ¹⁵NH₃ and ¹³CO₂ coupled with gravimetric measurements, we were able to determine total N and C uptake with repeated gas exposure. The hypotheses were: (i) a Lewis acid such as the C in CO₂ is strongly adsorbed to basic surfaces such as those of py-HSW, (ii) a Lewis base such as NH₃ is strongly retained by surface acidity created by this CO₂ adsorbed to py-HSW as well as by oxidizing pyrolyzed wood (py-ox wood), and (iii) alternating exposure to CO₂ and NH₃ increases the N retention capacity by refunctionalizing biochar surfaces to more acidic and more basic, respectively.

MATERIALS AND METHODS

Preparation of Ammonia Sorbents. Two types of feedstock, latrine waste or human solid waste (HSW) and maple wood chips (*Acer rubrum*), were converted into NH₃ sorbents through pyrolysis at 500 °C. The HSW collection process and the feedstock conversion process into biochars are outlined in the Supporting Information. Pyrolyzed maple wood was oxidized in H₂O₂ at a ratio of 1.6:10 g mL⁻¹ for 25 days, rinsed in deionized water (DIH₂O), and dried at 60 °C. Pyrolyzed HSW (py-HSW) was not oxidized. Prior to NH₃ or CO₂ exposure, both materials, py-HSW and pyrolyzed oxidized wood (py-ox wood), were degassed at 150 °C for 12 h under vacuum on a porosimeter (ASAP 2020, Micromeritics, Norcross, GA).

Experimental Procedure. Py-HSW and py-ox wood were exposed to pure NH₃ (10 atom % (AT %) $^{15}\rm{N}/^{14}\rm{N})$ and pure CO₂ $(10 \text{ AT } \% {}^{13}\text{C}/{}^{12}\text{C})$ within a thermogravimetric analyzer (TGA; Q50 EGA furnace, TA instruments) in different sequences described below and outlined in the Supporting Information. Our aim was to determine whether exposure to CO₂ can enhance NH₃ uptake in a material already enriched in amine functional groups. For this, we evaluated total N uptake from NH3 and N bonding structures in two materials exposed to CO_2 (1) py-HSW, which is characterized by inherent surface basicity due to amine functional groups, and (2) pyox wood artificially enriched with amine functional groups through NH₃ adsorption. We compared the effect of CO₂ conditioning of py-HSW on its N uptake with that of py-ox wood exposed to NH₃, which generated a material with similar N contents yet low ash content. The effectiveness of CO₂ in renewing the surface affinity for NH₃ was evaluated by repeatedly exposing our model material, py-ox wood sorbed with NH₃, to CO₂ followed by NH₃. Five types of gas exposure regimes were employed in triplicate: (1) py-HSW not exposed to gas (control), (2) py-HSW exposed to ${}^{13}CO_2$ for 1 h followed by ${}^{15}NH_3$ for 1 h (py-HSW CO₂ + NH₃), (3) py-ox wood not exposed to gas (control), (4) py-ox wood exposed to ¹⁵NH₃ for 1 h (py-ox wood NH_3), (3) py-ox wood exposed to ¹⁵ NH_3 for 1 h followed by ¹³ CO_2 for 1 h followed by ¹⁵NH₃ for 1 h followed by ¹²CO₂ for 1 h followed by ¹⁵NH₃ for 1 h followed by ¹³CO₂ for 1 h (py-ox wood NH₃ + CO₂) (Table S1). After each type of gas exposure, the TGA was purged with argon for 1 h. The weight of adsorption from gas exposure was calculated as the difference between the end weight after the final argon purge and the initial weight of the degassed sample, prior to CO₂ or NH₃ exposure.

Material Characterization. Heat of Adsorption. The effect of amine functional groups on CO_2 uptake was determined by measuring the heat of adsorption (Q_{st}) of CO_2 to py-HSW and py-ox wood before and after exposure to NH₃. Samples were exposed to unlabeled NH₃ for 1 h within a TGA at 30 °C. Three adsorption isotherms were measured at three temperatures: 0, 25, and 35 °C on a porosimeter (model-ASAP 2020, Instrument Corp., Norcross, GA) (Figure S1), and details on Q_{st} measurements are provided in the Supporting Information.

Enthalpic profiles showing the Q_{st} as a function of CO₂ surface coverage (θ) at a given temperature and pressure (P, T) were calculated for py-ox and py-HSW with the Clausius Clapeyron

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Figure 1. Thermodynamics and kinetics of CO_2 and NH_3 adsorption onto py-HSW and py-ox wood. (A) Enthalpic profile showing the heat of adsorption before and after exposure to CO_2 followed by NH_3 . The uncertainty associated with the heat of adsorption calculations is represented by shaded regions. (B) Thermograms depicting the weight change of the first replicate of py-HSW and py-ox wood exposed to CO_2 (orange) followed by NH_3 (blue), separated by an argon purge (gray). (C) The first replicate of gravimetrically measured CO_2 and NH_3 adsorption at three sequential exposure intervals in py-ox wood (indicated in gray, orange, and blue lines for intervals 1, 2, and 3, respectively) overlaid with modeled adsorption curves using Avrami's fractional order model (indicated by solid, narrow dashed, and wide dashed lines for intervals 1, 2, and 3, respectively). (D) The first replicate of gravimetrically measured CO_2 and NH_3 adsorption divertically measured adsorption curves using Avrami's fractional order model (black line). Avrami's model parameters are presented in Table S2; measured and modeled gravimetric CO_2 and NH_3 adsorption is presented in Figure S3 in the Supporting Information.

equation (eq 1) (MicroActive software, Version 4.06 (9f8ab05), Micromeritics Instrument Corp., Norcross, GA). Calculations performed within MicroActive include a Q_{st} uncertainty range for each degree of surface coverage and are represented in Figure 1 by a gray shaded band.

$$\frac{\Delta H_{\text{ads}}}{R} = \left(\frac{\partial \ln P}{\partial 1/T}\right)_{\text{const }\theta} \to -\Delta H_{\text{ads}} = \left[\frac{RT_1T_2}{T_2 - T_1} \times \ln\left(\frac{p_2}{p_1}\right)\right]_{\text{const }\theta}$$
(1)

Adsorption Kinetics. Avrami's fractional order model (eq 2) was used to describe adsorption of CO_2 and NH_3 onto py-ox wood and py-HSW

$$q_t = q_e [1 - e^{-(k_A t)^{n_A}}]$$
(2)

The model describes measured CO_2 sorption (q_i) over time (t) as a logarithmically increasing function of the equilibrium adsorption (q_e) , the rate parameter (k_A) , and the exponent (n_A) . Originally developed to model phase transitions and crystal growth, the Avrami model has been recently applied to describe CO_2 adsorption onto amine-functionalized surfaces.^{38,39} The materials used in this research are comparable to amine-functionalized surfaces on account of the ambient N enrichment of py-HSW and the artificial enrichment of py-ox wood through the first exposure to NH₃.

We also evaluated the performance of the Avrami model in describing NH_3 uptake. We inversely solved for shape parameters k_A and n_A through regression using eq 3, the linearized version of eq 2 (Table S2). Further information regarding adsorption kinetics is provided in the Supporting Information.

$$\ln\left(-\ln\left(1-\frac{q_t}{q_e}\right)\right) = n\ln(k) + n(\ln t)$$
(3)

Fourier Transform Infrared (FTIR) Spectroscopy. Functional group chemistry was analyzed with attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) on a Vertex 70 FTIR spectrometer (Bruker Corp., Billerica, MA) equipped with a deuterated L-alanine-doped triglycine sulfate (DLaTGS) detector. Powdered samples were automatically scanned 64 times in the midinfrared region from 4000 to 550 cm⁻¹ with a resolution of 4 cm⁻¹. Atmospheric correction was performed using OPUS 7.2 (Bruker Corp., Billerica, MA) while normalization was carried out in R studio,⁴⁰ as described in the Supporting Information.

To determine changes in functional group chemistry between unexposed "control" samples, py-HSW and py-ox wood, and samples exposed to NH_3 or $NH_3 + CO_2$, difference spectra were calculated. For the difference method, samples exposed to NH_3 or $NH_3 + CO_2$ are normalized relative to the minimum and maximum values of respective control samples. Wavenumber assignments and functional group assignments⁴¹ are presented in the Supporting Information (Table S3).

Isotope Ratio Mass Spectrometry by Combustion. Total $\rm NH_3-N$ and $\rm CO_2-C$ uptake were determined using isotope ratio mass spectrometry (IRMS), based on total C and N stoichiometry, AT % $^{13}\rm C/^{12}\rm C$ and AT % $^{15}\rm N/^{14}\rm N$ ratios, and changes in sample mass before and after gas exposure. Subsamples from each experimental treatment were ground and weighed into tin capsules. Total $^{12,13}\rm C$ and $^{14,15}\rm N$ of samples were measured by combustion on an isotope ratio mass spectrometer (Thermo Finnigan MAT Delta Plus, Thermo Electron Corporation, Waltham, MA) coupled to an elemental analyzer (NC2500, Carlo Erba, Egelsbach, Germany). To assure complete combustion, less than 0.5 mg of the sample was mixed with the 3-fold greater weight of vanadium pentoxide (Sigma-Aldrich, St. Louis, MO).

Nitrogen and C uptake were calculated according to eq 4 (shown for N), relying on the 15,14 N and 13,12 C AT % of samples before and after gas exposure and the AT % of gas cylinders.

Nanoscale Secondary Ion Mass Spectrometry. The co-location of ¹⁵N and ¹³C in samples before and after exposure to NH₃ and CO₂ was spatially resolved using nanoscale secondary ion mass spectrometry (NanoSIMS; Cameca NanoSIMS 50L, Gennevilliers Cedex, France). Measurements were carried out at the Environmental Molecular Sciences Laboratory of the Pacific Northwest National Lab (EMSL-PNNL). Samples were measured as whole particles within the identical size range used for adsorption experiments, 150–850 μ m. To achieve flat topography, particles were pressed with a glass slide into indium foil covering silicon wafers. All samples were sputter-coated with 15 nm of iridium to minimize charging.⁴²

Secondary ions were measured after high-current Cs⁺ sputtering, ~1.2 pA, at a dosing rate of 2×10^{16} ions cm⁻², to assure that sputtering equilibrium was achieved.^{42,43} Secondary ions ${}^{12}C^{12}C^{-}$, ${}^{12}C^{13}C^{-}$, ${}^{12}C^{14}N^{-}$, and ${}^{12}C^{15}N^{-}$ were measured. Sputter time was converted to sputtered depth⁴⁴ using eq 5.

sputterered depth(nm)

$$= \frac{\text{sputter rate } (\text{nm } \mu \text{m } \text{pA}^{-1} \text{ s}^{-1}) \times \text{Cs}^{+} \text{ beam } (\text{pA}) \times \text{sputter time(s)}}{\text{beam area } (\mu \text{m})}$$
(5)

Additional information on the NanoSIMS analysis is presented in the Supporting Information.

Near-Edge N-ray Absorption Fine Structure. The N K-edge bonding environment of py-ox wood and py-HSW before and after gas exposure was measured with near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, conducted at the Canadian Light Source SGM beamline in Saskatoon, Canada. Partial fluorescence counts were normalized by the beamline incidence flux on a gold mesh⁴⁵ using Jupyter Notebook software (Jupyter Notebook, IPython Project, 2014).^{46,47} Normalized spectra were deconvoluted into constituent N species through iterative fitting to curves associated with known N-containing compounds^{26,29,48,49} with Fityk software (Fityk 0.9.8).⁵⁰ Peak assignments for N form in standard compounds²⁶ and are presented along with the sample analyses and deconvolution method in the Supporting Information (Table S4).

X-ray Photoelectron Spectroscopy (XPS). Surface C, N, and O bonding structures on the whole particle were determined using X-ray photoelectron spectroscopy (XPS). While the probing depth for XPS is approximately 10 nm, electrons reaching detectors are from the first few atomic layers. Measurements were carried out at EMSL-PNNL using a Physical Electronics Quantera scanning X-ray microprobe (Physical Electronics, a division of ULVAC PHI). Spectral deconvolution was based on peak assignments for C, N, and O forms in five standard compounds: ammonium carbonate $((NH_4)_2^{2+}CO_3^{2-})$, ammonium bicarbonate $(NH_4^{+}HCO_3^{-})$, urea, proline, and valine (Figure S2, Tables S5 and S6), along with online and published literature.^{51–55} Instrument specifications and data analyses are presented in the Supporting Information.

Statistical Analysis. Data analyses were carried out with $ggplot2^{56,57}$ within R Studio.⁴⁰ Significant differences (p > 95%) in C and N uptake between py-HSW and py-ox wood were calculated using a *t*-test with the lm() function and associated summary.lm() method. Significant differences between samples were marked with a compact letter display of pairwise comparisons, calculated with the Tukey method for comparing a family of three estimates within the cld() function in the multcomp package.⁵⁸ The kinetics of CO₂ and NH₃ adsorption were modeled using the nonlinear regression function nls(). Additional R packages employed for this work are listed in Table S7.

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RESULTS

Thermodynamics and Kinetics of Adsorption. Containing 4.6% (w w⁻¹) total N, py-HSW is naturally enriched in organic N⁵⁹ even before exposure to NH₃. Py-ox wood can be artificially enriched with N following a single NH₃ exposure event (py-ox wood NH₃), during which the total N content increased from 0.21 to 3.74% (w w⁻¹). Materials naturally enriched (py-HSW) and artificially enriched (py-ox wood NH₃) with amine functional groups reached the CO₂ chemisorption threshold, 50 (kJ mol⁻¹),^{60,61} as shown by the CO₂ Q_{st} of py-HSW, 49.4 (kJ mol⁻¹) and py-ox wood exposed to NH₃, 50.4 (kJ mol⁻¹) (Figure 1A). The sorbed CO₂ facilitated NH₃ uptake in py-HSW, as observed by the 4.3% increase in sample weight corresponding to the uptake of 3.69 mg N g⁻¹ during NH₃ adsorption (Figures 1B and S3A). Argon purges (gray line) lowered the weight, but never to the stable, degassed weight.

The CO₂ "priming" or "regeneration" mechanism appears repeatable, as observed by the weight increase in py-ox wood following repeated exposure to CO₂ followed by NH₃. The end weight of our model sorbent, py-ox wood $NH_3 + CO_2$, exposed to three cycles of NH_3 (1 h) followed by CO_2 (1 h) was 14% greater than the degassed initial weight. The weight increase in py-ox wood was of a similar magnitude after each CO₂ exposure interval, 4.8% (w w⁻¹). Exposure of py-ox wood to NH₃ had a greater effect on the sample weight than exposure to CO2, but the magnitude of weight increase with NH3 exposure decreased with repeated exposure, from 8.9% (w w^{-1}) after the first exposure to 5.5% (w w^{-1}) after the third exposure. Gravimetrically measured NH₃ adsorption to py-HSW was 2.4-fold less $(3.7\% \text{ w s}^{-1})$ than in py-ox wood sorbed with NH₃ for the first exposure due to the lower CO₂ surface coverage within py-HSW, in spite of the high $CO_2 Q_{st}$ of the material (Figures 1 and S3B,C). Thus, in principle, the CO₂ regeneration mechanism on basic, amine-rich surfaces increased subsequent NH₃ adsorption but was lower in py-HSW than in py-ox wood.

A good fit of the fractional order Avrami model was observed for CO₂ adsorption in both py-HSW and py-ox wood (Figure 1C,D; Table S2, and Figure S3B,C). Values for the shape parameter n_A were lower than unity for all CO₂ exposure events, 0.54–0.85, in a similar range as reported for CO₂ sorption onto a zeolite bed.⁶² While the fit of the Avrami model was also good for NH₃ sorption, it was unable to model continued NH₃ sorption on py-ox wood after the first exposure event, but rather leveled off at a plateau.

Isotope Ratio Mass Spectrometry. Total N uptake was 1.5-fold greater in py-ox wood exposed to three intervals of $NH_3 + CO_2$ than py-ox wood only exposed once to NH_3 (py-ox wood NH_3), 40.57 (mg g⁻¹) vs 27.04 mg g⁻¹ (Table 1). The molar ratio of N/C uptake in py-ox wood exposed to three intervals of $NH_3 + CO_2$ was 4.99 mol N mol C⁻¹, while that in py-HSW exposed to one interval of $CO_2 + NH_3$ was only 0.79 mol N mol C⁻¹.

The extent of ¹⁵N isotope enrichment between py-ox wood and py-HSW corroborated gravimetrically measured adsorption (Table 1 and Figure 1B). NanoSIMS measurements across ROIs and depth profiles for a single ROI revealed an order of magnitude greater ¹⁵N uptake in both py-ox wood exposed only to NH₃ and py-ox wood exposed to three intervals of NH₃ + CO₂ (15 145–19 094‰), compared to py-

± 7.87 (a)

6.97

n/a

 -26.01 ± 0.04

 -25.7 ± 0.01

 -25.36 ± 0.07

 1.10 ± 0.00 1.10 ± 0.00

 $^{12}C + ^{13}C$ uptake (mg g⁻¹)

 4.02 ± 1.36 (a)

 -18.71 ± 1.11 -22.93 ± 0.13

 1.11 ± 0.00

 45.88 ± 0.73 44.04 ± 0.66

 1.11 ± 0.00 1.10 ± 0.00

 67.35 ± 5.02

 40.57 ± 13.69 (a) 27.04 ± 7.31 (a)

 18228 ± 2928

 0 ± 0

 20848 ± 5987

 7.38 ± 1.90

 3.74 ± 0.68

 4.29 ± 0.72

 14.7 ± 0.30

py-ox wood NH₃ + CO₂

py-ox wood NH₃

py-ox wood

 0.21 ± 0.01

 4.05 ± 0.80

 0.38 ± 0.00

 23 ± 2

'n/a, not applicable. ^bLetters represent greater than 95% probability of mean differences, p < 0.05.

 71.48 ± 0.24 74.13 ± 1.73

 δ^{13} C vs VPDB

AT % ¹³C/¹²C

 $\begin{array}{c} total \ C \\ (\% \ w \ w^{-1}) \end{array}$

 $^{14}N + {}^{15}N$ uptake (mg g⁻¹)

 $\delta^{15} \mathrm{N}$ vs at. air

 ${
m AT}_{15}^{\rm N}{
m N}^{14}{
m N}$

 $\begin{array}{c} total \ N \\ (\% \ w \ w^{-1}) \\ 5.33 \pm 0.13 \end{array}$

mass change $(\% \text{ w } \text{w}^{-1})$

 2.36 ± 0.65

py-HSW CO₂ + NH₃

py-HSW

sample

 1860 ± 249

 1.04 ± 0.09

 0.39 ± 0.00 6.57 ± 0.93

 4.57 ± 0.04

 $3.69 \pm 0.56 (b)$

HSW exposed to CO_2 + NH₃ (2,635‰) (Figure 2A,B; Table S8 and Figures S4–S9).

Enrichment of ¹⁵N in py-ox wood following exposure to ¹⁵NH₃ did not diminish with sputtering depth, even at the micron scale, and remained greater than 15,000%₀ at a minimum depth of 7.5 μ m (Figure 2A). Evidence for CO₂ uptake, observed in gravimetric measurements, was less apparent by the IRMS data because of the relatively high natural enrichment levels of ¹³C/¹²C (1.10–1.11 AT %) compared to ¹⁵N (0.38–0.39 AT %) for both py-ox wood and py-HSW (Table 1). No trend in ¹³C enrichment with sputtering depth was evident for py-ox wood or py-HSW samples exposed to NH₃ + CO₂ (Figure 2B; Table S8 and Figure S4).

Spectroscopic Investigation of the Nitrogen and Carbon Bonding Environment. FTIR. The adsorption peak at 1040 cm⁻¹ in the py-HSW spectra confirms the presence of amines⁴¹ (peak #7 in Figure 3A and Table S3), which, in addition to other factors such as oxidation of alkali metals, contributes to surface alkalinity, as shown by its pH of 10.3 in water (Table S9). We have ruled out silicon or clay minerals as the interpretation for this peak, contrary to their presence reported for animal manures⁶³ and compost teas;⁶ HSW was freshly collected from waste buckets and had not been mixed with soil or residual plant material. Moreover, no silicon was detected in wide-scan XPS spectra of milled py-HSW, while a prominent N peak was evident (Figure S10). We have also ruled out ethers or primary alcohols (C-O stretch), which are more common in woody biochars.⁶⁵ Corroborating our interpretation, a peak at 1082 cm⁻¹ has previously been interpreted as NH3 adsorbed to Lewis acid sites in oxidized graphene.¹

We expected a high affinity between the basic amine surface functional groups in py-HSW and CO₂, the central C atom of which behaves as a Lewis acid in binding with the free electron pair on N in amine functional groups.^{66,67} In contrast to py-HSW, py-ox wood has an acidic pH (3.8 in H₂O; Table S9), low total N content (0.21% w w⁻¹), and strong IR absorbance in regions corresponding to acidic functional groups such as carboxyls at 1709 cm⁻¹ (peak #2) and phenols at 1215 cm⁻¹ (peak #6) (Figure 3A and Table S3). The high affinity between acidic surface functional groups in py-ox wood and the Lewis base NH₃ was therefore expected.

FTIR difference spectra rather than nondifference spectra provided a clearer distinction of chemical changes in py-ox wood and py-HSW following exposure to NH₃ or NH₃ + CO₂. Following exposure of py-HSW to CO₂ + NH₃, a decrease in the secondary NH amine bend at 1570 cm⁻¹ (peak #3) and the tertiary aromatic amine CN stretch at 1362 cm⁻¹ was observed in the difference spectrum (peak #5; Figure 3A and Table S3). These amine functionalities are binding sites for CO₂. Peak #3 appears right shifted in the nondifference spectrum for py-HSW CO₂ + NH₃, causing the dip in the position of peak #3 in the py-HSW difference spectrum. The appearance of peak #4 at 1435 cm⁻¹ in the py-HSW CO₂ + NH₃ difference spectrum indicates the presence of NH₄⁺.

Unlike the difference spectrum for py-HSW $CO_2 + NH_3$, peak positions #3 and #5 were sharp and prominent for py-ox wood NH_3 . In the py-ox wood nondifference spectrum, peak #3 lies just right of and on the shoulder of the C=C-C aromatic ring stretch peak (1615–1580 cm⁻¹). The shoulder to the left of peak #3 in the nondifference spectrum of py-ox wood NH_3 and py-ox wood $CO_2 + NH_3$ is likely an overlap of

Table 1. Total N and C Uptake in py-ox Wood and py-HSW Before and After Exposure to NH₃ or NH₃ + CO₂. Calculated from Sample AT % ¹⁵N/¹⁴N and AT % ¹³C/¹²C Ratios, Accounting for the Change in the Sample Mass (Equation 4) a,b

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Figure 2. Delta ratios with sputtering depth showing the extent of ¹³C and ¹⁵N enrichment in (A) three replicate samples of py-ox wood and (B) three replicate samples of py-HSW before and after exposure to NH_3 or $NH_3 + CO_2$. The marker color differentiates between gas exposure treatments (blue = py-HSW $CO_2 + NH_3$ and py-ox wood $NH_3 + CO_2$; yellow = py-ox wood NH_3 ; and brown = unexposed py-HSW and py-ox wood), while the marker shape shows differences in measurements in replicate ROIs (circle = 1st replicate; triangle = 2nd replicate; and square = 3rd replicate). Replicate measurements are displayed individually in the Supporting Information (Figure S4).



Figure 3. (A) Normalized ATR-FTIR absorbance spectra of powdered samples. Difference spectra (diff.) were normalized relative to controls, py-HSW or py-ox wood. Numbered peak features are explained in Table S3. (B) Normalized N K-edge NEXAFS spectra of experimental samples. Points show measured spectra, while the black line is the modeled spectra after deconvolution. Features marked with dotted lines and numbers and relative area of Gaussians used for deconvolution are provided in Table S4. (C) Normalized intensity of counts within C 1s, N 1s, and O 1s regions of experimental samples, measured with XPS. Points show measured spectra, while the black line is the modeled spectra after deconvolution. Features marked with dotted lines and numbers and relative areas of peaks used for deconvolution are provided in Table S6.

the C=C-C aromatic ring stretch and newly incorporated amines (NH bend; 1650–1550 cm⁻¹). Also noteworthy is the disappearance of peaks #2 and #6 in py-ox wood NH₃ and py-ox wood NH₃ + CO₂ nondifference spectra, corresponding to carboxylic acid and Lewis acid phenol that serve as NH₃ binding sites.

NEXAFS. Exposure of py-ox wood to NH_3 created new spectral features in the N K-edge not detectable in unexposed

samples (Figure 3B). The lack of features in the corresponding N 1s XPS spectra (Figure 3C) for unexposed py-ox wood may indicate significant noise in the NEXAFS N K-edge spectra due to low N contents of 0.21% (w w⁻¹) (Table 1). The 18-fold increase in total N upon exposure of py-ox wood to NH₃ $(3.74\% \text{ w w}^{-1})$ and NH₃ + CO₂ $(4.05\% \text{ w w}^{-1})$ engendered the formation of protonated amines at 397.27 eV^{68,69} (peak #1), new pyridinic compounds at 398.76 eV, 399.54-399.81 eV, and 404.11 eV (peak #3,5,11), and new pyrroles at 402.40 eV (peak #9, Figure 3B, Tables S10 and S11). Repeated exposure of py-ox wood to CO₂ following NH₃ introduced one new spectral feature compared to py-ox wood exposed only once to NH₃, namely, keto-substituted pyridine rings at 399.20 eV (peak #4). Following exposure of py-ox wood to NH₃ and $NH_3 + CO_2$, the proportion of pyridinic N decreased by 18-22%, while the proportion of pyrrolic N increased by 48–52%. The proportion of N in primary amines bonded to pyridinic rings increased by 10-12%.

Diverse N species were detected in unexposed py-HSW, including pyridines (peak #2, 3, 5, and 11), keto-substituted pyridine rings (peak #7), pyrroles (peak #6,8,9), and amines (peak #10). Pyridinic N increased by 8% after py-HSW was exposed to CO_2 + NH₃, pyrrolic N decreased by 5%, and amine-substituted pyridine decreased by 19% (Tables S10 and S11). In contrast to py-ox wood, no new spectral features appeared after exposure of py-HSW to CO_2 and NH₃.

XPS. Significant N uptake on py-ox wood surfaces exposed to NH₃ and NH₃ + CO₂ was apparent from the sizable N 1s peaks in the XPS spectra collected from exposed samples compared to XPS spectra collected from unexposed py-ox wood. Pyridinic N (peak #14, 15) comprised more than 21% of the curve area in spectra collected from both py-ox wood NH₃ and py-ox wood NH₃ + CO₂, indicating the formation of heterocyclic N compounds with NH₃ exposure (Tables S12 and S13). Additionally, 56–60% of N forms in these samples were detected as electrostatically sorbed N (C–O–NH₄⁺) and 12–17% as NH₄⁺. As no KCl extraction was performed due to the limited sample size, the XPS-based assessment of electrostatically sorbed NH₄⁺ is putative.

The center of the N 1s spectrum for py-ox wood exposed to both $NH_3 + CO_2$ (399.8 eV) is shifted toward higher energies compared to py-ox wood exposed to only NH_3 (399.3 eV). The contribution of a Gaussian curve representing primary amine compounds (C-NH₂, 399.0-399.5 eV) shifts the N 1s curve center for py-ox wood NH₃ to lower energies. Pyridinic N (peak #14,15) and aromatic N bonded to ketone groups (peak #11) comprised over 44% of N in unexposed py-HSW surfaces. Traces of mineral N as NH_4^+ were also evident, comprising about 7% of the initial N compounds in py-HSW. Following exposure of py-HSW to $CO_2 + NH_3$, three new features appear, nonaromatic amidic N (peak #10), electrostatically sorbed NH_4^+ (peak #12), and amine-N (peak #13).

Carbon 1s peaks were identical for py-HSW before and after exposure to $CO_2 + NH_3$, showing a large C==C feature (peak #6) and smaller contributions from C-N (peak #5) and C-O (peak #4). Amide peaks (peak #1) increased 2.8-fold in py-HSW $CO_2 + NH_3$ compared to py-HSW. Spectral variation in the C 1s energy region is more evident in py-ox wood before and after exposure to NH₃ and between py-ox wood exposed to NH₃ and NH₃ + CO₂. The curve associated with C-N (peak #5) is largest in py-ox wood NH₃, while the higherenergy C==C (peak #2) is greatest for py-ox wood exposed to NH₃ + CO₂. The upward slant in O 1s peaks for py-ox wood exposed to NH₃ and NH₃ + CO₂ is caused by an increase in C==O functionalities (peak #20) relative to C-O (peak #18).

DISCUSSION

Weight Increase through Adsorption. Adsorption of NH₃ and CO₂ caused a non-negligible weight increase in both py-ox wood and py-HSW. It was essential to account for the mass change to determine N and C uptake from NH₃ and CO₂ that could not be obtained with either elemental or isotope analyses. The weight gain originates from adsorption on outer surfaces as well as within micropores, as seen by the NanoSIMS depth profiles that reach at least ~7 μ m in depth. Despite the relatively low flow rate of gases within the TGA, gases penetrated into inner cavities.

The experimental conditions significantly affect the NH₃ adsorption obtained in different studies. The lower NH₃-N uptake in py-ox wood $NH_3 + CO_2$ in our study compared to that in differently oxidized py-ox wood based on their O/C ratios²⁶ (Table S14), 40.6 vs 90.3 mg N g^{-1} , can be explained by differences in time of exposure and pressure. NH₃ uptake to differently oxidized py-ox wood²⁶ was obtained under equilibrium conditions in a vacuum of 80-800 Torr at 35 $^{\circ}$ C. We did not reach NH₃ pressures corresponding to equilibrium adsorption and do not report potential NH₃ uptake, but rather N uptake under a specified flow rate and time of exposure. A similar magnitude of discrepancy in measured vs expected NH₃ uptake based on the O/C ratio was shown for 500 °C pine biochar exposed to NH₃ from a vaporizing ammonium sulfate solution.⁷⁰ Ammonia uptake on py-ox wood reported here, 8.4 mg N g⁻¹, was comparable to values reported for low-temperature woody biochar mixed into the soil and treated with cattle urine, 25 8.6 mg N g⁻¹ (the O/C ratio estimated based on its N and C values⁷⁰ and the ash content of a similar biochar⁷¹).

Effects of Surface Chemistry on Adsorption. Strong sorption of NH₃ on acidic functional groups such as carboxyl C is well documented in the literature, 10,67,72,73 as is chemisorption of CO₂ in liquid amines^{74,75} or onto aminefunctionalized scaffolds. 34,61,67,76 Unlike activated carbon, the materials studied here were not engineered for high surface area through physical or chemical activation⁷⁷ and therefore had lower surface coverage of CO₂. Nevertheless, surface chemistry of py-HSW, naturally enriched in amine functional groups, and py-ox wood, artificially enriched in amine groups following exposure to NH₃, facilitated strong Q_{stv} greater than 50 kJ mol⁻¹. Surface-stabilized CO₂ molecules within py-HSW and py-ox wood enhanced the surface affinity for new NH₃ molecules. Thus, for py-ox wood, each subsequent round of NH₃ + CO₂ exposure resulted in incremental N enrichment. While oxidized graphene or oxidized activated carbon can sorb greater quantities of N than our materials,^{22–24} our interest was the NH₃-enrichment potential of pyrolyzed waste, py-HSW, for use as a fertilizer, benchmarking its sorption against pyrolyzed and oxidized woody biomass as an upper threshold for N uptake of such materials.

The CO₂ heat of adsorption increased with increased surface coverage for py-HSW before and after NH₃ exposure and for py-ox wood after NH₃ exposure, unlike the expected trend for monolayer gas adsorption of noninteracting gas molecules. Varying degrees of a positive dependence of $Q_{\rm st}$ on surface coverage have been reported for amine-functionalized scaffolds.^{78–81} Adsorbate–adsorbate interactions indicative of increasing $Q_{\rm st}$ with increasing surface coverage⁸⁰ have been explained as the cooperative binding of CO₂ molecules, whereby a higher heat of adsorption for a second incoming CO₂ molecule is observed, if an adjacent binding site is occupied by a CO₂ molecule.^{78,79}

Altered Surface Properties with NH₃ and CO₂ Adsorption. The initial surface chemistry of unexposed pyox wood included carboxylic, ketone, and phenolic groups, promoting a high affinity for NH₃. When adding CO₂ after this NH₃ exposure, the appearance of C=N pyrimidine bound to a keto group (py-ox wood NH₃ + CO₂ in Figure 3B) demonstrates that CO₂ chemisorption on py-ox wood introduces C-moieties similar to those found in unexposed py-ox wood such as carboxylic and ketone groups. Furthermore, N compounds in py-ox wood after 1 h of NH₃ exposure were similar to N compounds generated after 3 h of NH₃ + CO₂. Thus, sequential exposure of py-ox wood to NH₃ and CO₂ resulted in an extension of the surface chemistry outward apparently without significantly introducing new functional group types.

We anticipated greater C (from CO₂ exposure) and as a consequence N uptake (from the subsequent NH₃ exposure) in py-HSW because of its high initial N content, 4.57% (w w^{-1}) or 3.26 mmol N g^{-1} , and because of the results from CO₂ exposure to py-ox wood than actually observed. If each CO₂ molecule is sorbed to a single amine or a pair of amines, C uptake would have been at a ratio of $0.5-1 \mod CO_2$ per mol initial N, 1.63–3.26 mmol CO_2 g⁻¹, or 19.6–39.2 mg C g⁻¹. If NH₃ uptake continued according to the molar C/N uptake ratio of 1.2 measured for py-HSW in Table 1, we would have expected 1.4–2.7 mmol N g^{-1} or 16.3–32.6 mg N g^{-1} . We suggest that the high ash content of py-HSW (39% w w^{-1}) compared to py-ox wood (0.7% w w⁻¹; Table S9) may have impeded access to pore spaces, lowering CO₂ uptake to 4.0% $(w w^{-1})$, far below expected values (Table 1). Reduced diffusion into pore spaces may have limited access of CO₂ to amine groups, also lowering the expected effect of CO₂ exposure on subsequent NH₃ uptake.

Furthermore, residual water in py-HSW coupled with a high ash content may have "consumed" CO_2 through formation of bicarbonates and subsequent ion pair reactions with ash minerals such as K⁺. Indeed, oxygen XPS spectra indicated that there were small amounts of H₂O in py-HSW before and after exposure to CO_2 + NH₃, even after degassing, but not in py-ox wood (Figure 3C and Table S12). Residual water has been shown to catalyze the formation of bicarbonate, ^{32,36,37,82} which

can interact with cationic species including NH_4^+ or K^+ . The molar ratio of NH_3 –N vs CO_2 –C uptake in py-ox wood NH_3 + CO_2 was 2-fold greater than in py-HSW CO_2 + NH_3 , even when considering the difference in the number of exposures (the repeated exposure of py-of wood decreases NH_3 uptake compared to CO_2). Taken together, these results suggest that HSW's high ash content may have reduced NH_4^+ adsorption following CO_2 exposure.

Metal Effects on CO₂ and NH₃ Adsorption. The increase in surface K⁺ concentrations of py-HSW following exposure to CO_2 + NH₃ is possible evidence of potassium bicarbonate ion pairs precipitating on the surface. XPS data revealed a 2.7-fold increase in the K 2p1 peak area of py-HSW exposed to CO2 + NH3 compared to unexposed py-HSW (Figure S11), as well as 4.5% AT greater surface K in py-HSW CO_2 + NH₃ compared to unexposed py-HSW (Table S14). Concentrations of other metals remained unchanged between py-HSW before and after exposure to $CO_2 + NH_3$. While bulk total K⁺ was unaffected by NH₃ and CO₂ exposure, it is possible that K⁺ ions within the HSW migrated to fill empty sites, as has been observed for crystalline solids such as glass.⁸ It is unclear whether the presence of HCO3⁻ created energetically favorable conditions for K⁺ migration to surfaces, although this may be the only explanation for the 4.5% AT point increase in surface K⁺ following CO₂ and NH₃ exposure. Thus, while repeated, sequential NH₃ uptake occurs in py-ox wood $NH_3 + CO_2$, the nature of CO_2 interactions with the ash fraction in py-HSW restricts NH₃ adsorption, as explained above in our estimated CO2-C and subsequent NH3-N uptake in py-HSW judging from initial N contents. Improved adsorption might be possible by leaching the ash from py-HSW, although rinsing with water will also lower phosphorus (P), K^+ , magnesium (Mg²⁺), and calcium (Ca²⁺) concentrations, possibly lowering the overall agronomic value of the fertilizer. Since the ash fraction in biochar generally increases with higher pyrolysis temperatures,^{30,71} lowering the pyrolysis temperature of HSW may provide an avenue to change adsorptive properties for CO₂ and subsequent NH₃.

CONCLUSIONS

Significant sequential adsorption of NH_3 followed by CO_2 is possible in solid porous sorbents made from organic waste materials under dry conditions. Sorption kinetics of py-ox wood demonstrated that surface affinity can switch between NH_3 and CO_2 , allowing for material accretion through repeated chemisorption. These insights may provide a path toward conversion of untreated HSW and NH_3 , volatilizing from urine into N-rich soil amendments by decentralized waste management systems. The combination of pyrolysis-based sanitation producing a biochar that can be exposed to CO_2 emitted during pyrolysis merits further evaluation as a retention pathway for NH_3 that can be returned to soil. The process of CO_2 and NH_3 accretion through gaseous chemisorption points to the possibility of growing a fertilizer.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.0c01427.

Method, conversion of wood chips and human solid waste into biochar, adsorption experiment with NH_3 and CO_2 , preparation of materials for heat of CO_2

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adsorption, fitting the Avrami model to adsorption data, FTIR spectral processing, processing of NanoSIMS data, NEXAFS spectral processing, XPS instrument settings and data analyses, Table S1, experimental treatment structure; Figure S1, adsorption isotherms of CO2 on py-HSW and py- ox wood before and after exposure to NH_3 at three temperatures 0, 25, and 35 °C; Table S2, Avrami model parameter values; Table S3, FTIR wavenumber range assignments; Table S4, nitrogen forms and corresponding Gaussian peak assignments for NEXAFS; Figure S2, normalized XPS spectra for standard compounds; Table S5, binding energies and full-width at half-maximum values of standard compounds used for the deconvolution model; Table S6, the binding energy assignments for XPS based on standard compounds; Table S7, R software packages used; Figure S3, thermograms of the weight of change with exposure to CO₂ and NH₃; Table S8, nanoscale secondary ion mass spectrometry ion ratios; Figure S4, isotopic enrichment at depth using NanoSIMS; Figure S5, NanoSIMS images of py-ox wood; Figure S6, Nano-SIMS images of py-ox NH₃; Figure S7, NanoSIMS images of py-ox wood NH₃ + CO₂; Figure S8, NanoSIMS images of py-HSW controls, unexposed to NH₃ or CO₂; Figure S9, NanoSIMS images of py-HSW CO₂ + NH₃; Table S9, chemical and physical properties of py-ox wood and py-HSW; Figure S10, wide-scan XPS spectra; Table S10, proportion of nitrogen bond forms determined by NEXAFS; Table S11, nitrogen forms measured with N K-edge NEXAFS and full-width at half-maximum values; Table S12, proportion of C, N, and O measured with XPS and determined from a deconvolution model using standards; Table S13, binding energies and full-width at half-maximum values of samples determined with XPS; Table S14, carbon, nitrogen, and oxygen contents determined by IRMS and XPS; Figure S11, narrow scan XPS spectra in the C 1s region; Supplementary references (PDF)

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Notes

The authors declare no competing financial interest.

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