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

Leilah Krounbi, Akio Enders, Christopher R. Anderton, Mark H. Engelhard, Rachel Hestrin, Dorisel Torres-Rojas, James J. Dynes, and Johannes Lehmann*

ABSTRACT: The amine-rich surfaces of pyrolyzed human solid waste (py-HSW) can be "primed" or "regenerated" with carbon dioxide (CO2) to enhance their adsorption of ammonia (NH3) for use as a soil amendment. To better understand the mechanism by which CO2 exposure facilitates NH3 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 CO2 and then resorbed NH3. The high heat of CO2 adsorption (Qst) on py-HSW, 49 kJ mol−1, at low surface coverage, 0.4 mmol CO2 g−1, showed that the naturally occurring N compounds in py-HSW have a high affinity for CO2. The Qst of CO2 on py-ox wood also increased after exposure to NH3, reaching 50 kJ mol−1 at 0.7 mmol CO2 g−1, demonstrating that the incorporation of N-rich functional groups by NH3 adsorption is favorable for CO2 uptake. Adsorption kinetics of py-ox wood revealed continued, albeit diminishing NH3 uptake after each CO2 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 affinity for CO2 exposure to NH3. We then exposed these N-enriched materials to CO2 and then resorbed NH3. 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 (CH2N2O), 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 (NH4+) and nitrate (NO3−) from liquid streams.8−15 Ammonia gas (NH3) 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 Brønsted base and as an electron-donating Lewis base.21,22 In the presence of water, NH3 adsorbs to solid sorbents electrostatically as NH4+.23 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.24 Hydrogen bonding between NH3 and oxygenated functional groups is another mechanism for NH3 adsorption.25 For this reason, oxidized carbonaceous substrates such as graphene oxide are excellent NH3 sorbents.26−28 

Dry scrubbing of NH3 has proven effective with oxidized graphene and activated carbon.29−31 Another option for sorbents, which combines the high adsorption potential of zeolites or activated carbon, is pyrolyzed biomass or biochar.32 Pyrolysis may convert straw, woody shrubs, and manure solids into porous, surface-functionalized adsorbents.33 As most biomass feedstocks are waste materials, they can be locally
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 NH3.25 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 physiosorption 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 NH3 sorbent, removing over 18 g N g−1 from NH4Cl solution. Moreover, poultry biochar sorbed slightly less NH4+ compared to wood biochar from NH4NO3 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.28 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 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.70 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 amino-sugar compounds instead of amino acids.30 These N-containing surface functional groups, primary, secondary, and tertiary amines, have properties of Lewis and Bronsted bases containing surface functional groups, primary, secondary, and tertiary 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 CO2 in the presence of water vapor to form bicarbonate.55 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 CO2 enhances the affinity for NH3 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 NH3 following a single pre-exposure to CO2. To determine the robustness of surface repriming with CO2 in facilitating NH3 uptake without potentially confounding effects of ash minerals, we artificially enriched an ash-poor sorbent with amine functional groups through exposure to NH3 and then evaluated whether repeated exposure to CO2 facilitates additional NH3 uptake. We chose a biomass-derived sorbent previously reported to have high NH3 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 (D2O), 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 %) 15N/14N) and pure CO2 (10 AT % 13C/12C) 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 CO2 (1) py-HSW, which is characterized by inherent surface basicity due to amine functional groups, and (2) py-ox 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.60 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-ox wood not exposed to gas (control), (2) py-ox HSW exposed to 13CO2 for 1 h followed by 15NH3 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 NH3), (5) py-ox wood exposed to 13CO2 for 1 h followed by 15NH3 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 CO2 uptake was determined by measuring the heat of adsorption (Qads) of CO2 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 Qads measurements are provided in the Supporting Information.

Enthalpy profiles showing the Qads 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
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 CO₂ (orange) followed by NH₃ (blue), separated by an argon purge (gray). (C) The first replicate of gravimetrically measured CO₂ and NH₃ 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 CO₂ and NH₃ adsorption onto py-HSW (blue line) overlaid with modeled adsorption curves using Avrami’s fractional order model (black line). Avrami’s model parameters are presented in Table S2; measured and modeled gravimetric CO₂ and NH₃ adsorption is presented in Figure S3 in the Supporting Information.

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 mid-infrared 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® 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 NH₃ or NH₃ + CO₂, difference spectra were calculated. For the difference method, samples exposed to NH₃ or NH₃ + CO₂ are normalized relative to the minimum and maximum values of respective control samples. Wavenumber assignments and functional group assignments are presented in the Supporting Information (Table S3).

Isotope Ratio Mass Spectrometry by Combustion. Total NH₃–N and CO₂–C uptake were determined using isotope ratio mass spectrometry (IRMS), based on total C and N stoichiometry, AT % ¹³C/¹²C and AT % ¹⁵N/¹⁴N ratios, and changes in sample mass before and after gas exposure. Subsamples from each experimental treatment were ground and weighed into tin capsules. Total ¹³C and ¹⁵N 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, Egelshach, 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 ¹⁵N/¹⁴N and ¹³C/¹²C AT % of samples before and after gas exposure and the AT % of gas cylinders.
RESULTS

Thermodynamics and Kinetics of Adsorption. Containing 4.6% (w w\(^{-1}\)) total N, py-HSW is naturally enriched in organic N\(^{15}\) even before exposure to NH\(_3\). Py-ox wood can be artificially enriched with N following a single NH\(_3\) exposure event (py-ox wood NH\(_3\)), 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 NH\(_3\)) with amine functional groups reached the CO\(_2\) chemisorption threshold, 50 (kJ mol\(^{-1}\))\(^{60,61}\) as shown by the CO\(_2\) Qs of py-HSW, 49.4 (kJ mol\(^{-1}\)) and py-ox wood exposed to NH\(_3\), 50.4 (kJ mol\(^{-1}\)) (Figure 1A). The sorbed CO\(_2\) facilitated NH\(_3\) 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 NH\(_3\) adsorption (Figures 1B and S3A). Argon purges (gray line) lowered the weight, but never to the stable, degassed weight.

The CO\(_2\) “priming” or “regeneration” mechanism appears repeatable, as observed by the weight increase in py-ox wood following repeated exposure to CO\(_2\) followed by NH\(_3\). 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 CO\(_2\) exposure interval, 4.8% (w w\(^{-1}\)). Exposure of py-ox wood to NH\(_3\) had a greater effect on the sample weight than exposure to CO\(_2\), but the magnitude of weight increase with NH\(_3\), 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 NH\(_3\) adsorption to py-HSW was 2.4-fold less (3.7% w w\(^{-1}\)) than in py-ox wood sorbed with NH\(_3\) for the first exposure due to the lower CO\(_2\) surface coverage within py-HSW, in spite of the high CO\(_2\) Qn of the material (Figures 1 and S3B,C). Thus, in principle, the CO\(_2\) regeneration mechanism on basic, amine-rich surfaces increased subsequent NH\(_3\) adsorption but was lower in py-HSW than in py-ox wood.

A good fit of the fractional order Avrami model was observed for CO\(_2\) 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 CO\(_2\) exposure events, 0.54−0.85, in a similar range as reported for CO\(_2\) sorption onto a zeolite bed.\(^{62}\) While the fit of the Avrami model was also good for NH\(_3\) sorption, it was unable to model continued NH\(_3\) 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 \(^{15}\)N 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 \(^{15}\)N uptake in both py-ox wood exposed only to NH\(_3\) and py-ox wood exposed to three intervals of NH\(_3\) + CO\(_2\) (15 145−19 094\%e), compared to py-
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)

<table>
<thead>
<tr>
<th>Sample</th>
<th>NH3 CO2 0.21%</th>
<th>NH3 CO2 0.72%</th>
<th>NH3 CO2 1.10%</th>
<th>NH3 0.38%</th>
<th>NH3 0.72%</th>
</tr>
</thead>
<tbody>
<tr>
<td>sample mass change (g%)</td>
<td>45.48 ± 0.73</td>
<td>40.04 ± 0.66</td>
<td>37.13 ± 0.71</td>
<td>27.04 ± 0.80</td>
<td>24.04 ± 1.01</td>
</tr>
<tr>
<td>AT %15N/14N</td>
<td>0.53 ± 0.13</td>
<td>0.59 ± 0.00</td>
<td>0.74 ± 0.04</td>
<td>0.63 ± 0.03</td>
<td>0.58 ± 0.02</td>
</tr>
<tr>
<td>AT %13C/12C</td>
<td>3.73 ± 0.30</td>
<td>3.74 ± 0.30</td>
<td>3.78 ± 0.30</td>
<td>3.78 ± 0.30</td>
<td>3.78 ± 0.30</td>
</tr>
</tbody>
</table>

HSW exposed to CO2 + 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‰ at a minimum depth of 7.5 μm (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).

3 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 amines\(^{41}\) (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 manures\(^{63}\) and compost teas;\(^{64}\) 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.\(^{17}\)

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 H\(_2\)O; 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 CO2 + NH3, peak positions #3 and #5 were sharp and prominent for py-ox wood NH3. 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 NH3 and py-ox wood CO2 + NH3 is likely an overlap of
Figure 2. Delta ratios with sputtering depth showing the extent of $^{13}$C and $^{15}$N 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 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 S6.

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, and #9), and amines (peak #10). Pyridinic N increased by 8% after py-HSW was exposed to CO$_2$ + NH$_3$, pyrrolinic 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 NH$_3$.

XPS. Significant N uptake on py-ox wood surfaces exposed to NH$_3$ and NH$_3$ + CO$_2$ was apparent from the sizable N 1s peak increases 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 NH$_3$ and py-ox wood NH$_3$ + CO$_2$, indicating the formation of heterocyclic N compounds with NH$_3$ exposure (Tables S12 and S13). Additionally, 56–60% of N forms in these samples were detected as electrostatically sorbed N (C–O–NH$_4^+$) and 12–17% as NH$_4^+$. As no KCl extraction was performed due to the limited sample size, the XPS-based assessment of electrostatically sorbed NH$_4^+$ 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–NH$_2$; 399.0–399.5 eV) shifts the N 1s curve center for py-ox wood NH$_3$ 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 NH₄⁺ were also evident, comprising about 7% of the initial N compounds in py-HSW. Following exposure of py-HSW to CO₂ + NH₃, three new features appear, nonaromatic amidic N (peak #10), electrostatically sorbed NH₄⁺ (peak #12), and amine-N (peak #13).

Carbon 1s peaks were identical for py-HSW before and after exposure to CO₂ + NH₃, 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 CO₂ + NH₃ 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 higher-energy 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 μm 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 NH₃ + CO₂ in our study compared to that in differently oxidized py-ox wood based on their O/C ratios, was obtained for py-HSW because of its high initial N content, 4.57% (w/w), and because of the results from CO₂ exposure to py-ox wood after NH₃ exposure, the appearance of C=O pyrolyzed waste, py-HSW, for use as a fertilizer, bench-marking 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 Qₐ on surface coverage have been reported for amine-functionalized scaffolds. Adsorbate–adsorbate interactions indicative of increasing Qₐ with increasing surface coverage 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.

**Altered Surface Properties with NH₃ and CO₂ Adsorption.** The initial surface chemistry of unexposed py-ox 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) 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 mol CO₂ per mol initial N, 1.63–3.26 mmol CO₂ 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) compared to py-ox wood (0.7% w/w) Table S9), may have impeded access to pore spaces, lowering CO₂ uptake to 4.0% (w/w), 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” CO₂ 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 CO₂ + 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, 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-ox 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 CO$_2$ and NH$_3$ Adsorption.** The increase in surface K$^+$ concentrations of py-HSW following exposure to CO$_2$ + NH$_3$ 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 CO$_2$ + NH$_3$ compared to unexposed py-HSW (Figure S11), as well as 4.5% AT greater surface K in py-HSW CO$_2$ + NH$_3$ 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 NH$_3$ and CO$_2$ exposure, it is observed that K$^+$ ions within the HSW migrated to fill empty sites, as has been observed for crystalline solids such as glass. It is unclear whether the presence of HCO$_3^−$ 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 CO$_2$ and NH$_3$ exposure. Thus, while repeated, sequential NH$_3$ uptake occurs in py-ox wood NH$_3$ + CO$_2$, the nature of CO$_2$ interactions with the ash fraction in py-HSW restricts NH$_3$ adsorption, as explained above in our estimated CO$_2$–C and subsequent NH$_3$–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 (Mg$^{2+}$), and calcium (Ca$^{2+}$) concentrations, possibly lowering the overall agronomic value of the fertilizer. Since the ash fraction in biochar generally increases with higher pyrolysis temperatures, lowering the pyrolysis temperature of HSW may provide an avenue to change adsorptive properties for CO$_2$ and subsequent NH$_3$.

**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$_2$ 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 CO$_2$ 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 CO$_2$ and NH$_3$; 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, NanoSIMS images of py-ox NH$_3$; Figure S7, NanoSIMS images of py-ox wood NH$_3$ + CO$_2$; Figure S8, NanoSIMS images of py-HSW controls, unexposed to NH$_3$ or CO$_2$; Figure S9, NanoSIMS images of py-HSW CO$_2$ + NH$_3$; 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)

**AUTHOR INFORMATION**

**Corresponding Author**

**Johannes Lehmann — Soil and Crop Sciences, College of Agriculture and Life Sciences and Atkinson Center for a Sustainable Future, Cornell University, Ithaca, New York 14853, United States; orcid.org/0000-0002-4701-2936; Email: CL273@cornell.edu**

**Authors**

**Leilah Krounbi — Soil and Crop Sciences, College of Agriculture and Life Sciences, Cornell University, Ithaca, New York 14853, United States**

**Akio Enders — Soil and Crop Sciences, College of Agriculture and Life Sciences, Cornell University, Ithaca, New York 14853, United States**

**Christopher R. Anderton — Environmental Molecular Sciences Laboratory, Pacific Northwest National Lab, Richland, Washington 99354, United States; orcid.org/0000-0002-6170-1033**

**Mark H. Engelhard — Environmental Molecular Sciences Laboratory, Pacific Northwest National Lab, Richland, Washington 99354, United States; orcid.org/0000-0002-5543-0812**
Rachel Hestrin — Soil and Crop Sciences, College of Agriculture and Life Sciences, Cornell University, Ithaca, New York 14853, United States
Dorisel Torres-Rojas — Soil and Crop Sciences, College of Agriculture and Life Sciences, Cornell University, Ithaca, New York 14853, United States
James J. Dynes — Canadian Light Source, Saskatoon, SK S7N 2V3, Canada; orcid.org/0000-0002-5727-530X

Complete contact information is available at: https://pubs.acs.org/10.1021/acssuschemeng.0c01427

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was funded by the NSF IGERT Food Systems and Poverty Reduction (grant 0903371), the Bill and Melinda Gates Foundation (Reinvent the Toilet Program, grant OPP1069565), NSF-BREAD (grant IOS-0965336), the Bradford Research Award (grant number 1258485), USDA Hatch (NYC-125443, NYC-125314), and SARE (GNE17-154). This work made use of the Cornell Center for Materials Research Shared Facilities that are supported through the NSF MRSEC program (DMR-1719875), and a portion of this research was performed in the W.R. Wiley Environmental Molecular Sciences Laboratory (EMLS), a national scientific user facility sponsored by the Office of Biological and Environmental Sciences (BER) and located at the Pacific Northwest National Lab (PNNL). Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the donors. The authors thank Kelly Hanley for help in characterizing biochars and in experimental design. They also thank Dr. Michael Schmidt for assistance with FTIR, Professor Frank DiSalvo for access to laboratory facilities, Professor Murray McBride for assistance in experimental concepts, and Erika Mudrak at the Cornell Statistical Consulting Unit for assistance. They also thank Dr. Jeff Kevin at Micromeritics for assistance in conducting CO₂ adsorption isotherms and interpreting the data. The authors are also grateful for the tremendous help provided by the helpline staff at TA instruments, particularly Carmen Zambeno. The authors also acknowledge the staff at Sanergy in Nairobi, Kenya, for their collaboration, specifically Fausto Marcigot in the collection and pyrolysis of HSW.

■ REFERENCES

(27) Bai, X.; Li, Z.; Zhang, Y.; Ni, J.; Wang, X.; Zhou, X. Recovery of ammonium in urine by biochar derived from faecal sludge and its...


(75) Kortunov, P. V.; Baugh, L. S.; Siskin, M.; Calabro, D. C. In situ nuclear magnetic resonance mechanistic studies of carbon dioxide reactions with liquid amines in mixed base systems: The interplay of Lewis and Bronsted basicsities. *Energy Fuels* 2015b, 29, 5967−5989.


