Data Article

Characterization data of N-doped biochars using different external nitrogen precursors

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ABSTRACT

The development of waste-derived functional materials for environmental and energy applications is a sustainable approach to fight global warming, and address energy and materials challenges. In this regard, many scientists are interested in the supercapacitor, adsorbent, and catalyst applications of nitrogen-doped biochars. In this article, we report the data that was collected as a part of our research on the effects of different external nitrogenous sources on the properties of biochar [1]. The data on infrared spectra of the modified samples at various temperatures is valuable to study the changes in functional groups on biochar as a function of temperature as well as nitrogen precursors. Raw data from Time-of-flight Secondary ion mass spectroscopy, surface profilometry, and scanning electron microscopy-energy dispersive X-ray spectroscopy are also provided. We expect that the data will benefit researchers around the world working in the field of nitrogen modifications of biochar.

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Specifications Table

| Subject                  | Agricultural, Environmental, and Chemical Engineering |
|--------------------------|------------------------------------------------------|
| Specific subject area    | Waste management through the development of functional carbon materials from wastes |
| Type of data             | Data point table (dpt) files                         |
|                          | Text files                                           |
|                          | Images                                               |
|                          | Spreadsheet                                          |
| How data were acquired   | Variable Pressure Scanning Electron Microscope-EDX (Hitachi S-3200 N), Time-of-Flight-Secondary Ion Mass Spectroscopy (ToF-SIMS) (ION TOF, Inc.), Confocal laser scanning microscope (CLSM, Keyence VKx1100), Bruker Platinum ATR spectrometer |
| Data format              | Raw and processed data                               |
| Parameters for data collection | The pine bark samples were used as received. The prepared biochar samples were stored at room temperature in an air-tight container. |
| Description of data collection | Infrared spectra of the biochar samples were obtained using a Bruker Platinum ATR spectrometer. Time-of-Flight-Secondary Ion Mass Spectroscopy (ToF-SIMS) (ION TOF, Inc.) technique was used to obtain high-resolution spectral images. Surface profile data was obtained using a Confocal laser scanning microscope (CLSM, Keyence VKx1100). EDX images were obtained using a Variable Pressure Scanning Electron Microscope-EDX (Hitachi S-3200 N). |
| Data source location     | North Carolina State University, Raleigh, NC, USA. |
| Data accessibility       | All the associated data are available at Kasera, Nitesh; Hall, Steven; Kolar, Praveen (2021), “Characterization data of Nitrogen-doped pinewood biochars”, Mendeley Data, V1, doi: 10.17632/663dfg589z.1 |
| Related research article | N. Kasera, P. Kolar, S. Hall, Effect of different nitrogen precursors on morphology and surface chemistry of pine bark biochar, Journal of Environmental Chemical Engineering, submitted along with this manuscript. https://doi.org/10.1016/j.jece.2021.105161 |

Value of the Data

- Pine bark has a significant potential to be used as a precursor for producing multifunctional carbon materials.
- Researchers working in the field of waste management, functional carbon materials, and energy storage may find these data useful.
- The data presented here can be used to draw important insights about the properties of biochars upon nitrogen modification which can be exploited to produce application-specific materials.

1. Data Description

Pine bark biochar was modified with melamine, urea, ammonium chloride, and ammonium nitrate. The modified biochar samples were analyzed to obtain structural and morphological information. The data reported here are raw and researchers may plot and interpret the data as they deem fit. Fig. 1 shows the infrared spectra for modified biochar samples at different temperatures (500–800°C). The position and intensities of the peaks change with precursors and temperatures. With the increase in temperature, the peaks are diminished. Raw data point files (DPT) are attached for all the shown spectra which can be converted into excel for plotting. Infrared spectra for pristine biochar and modified biochar samples at 400°C are reported in the associated manuscript [1].

Fig. 2 shows the negative ion ToF-SIMS spectra for urea, ammonium chloride, and ammonium nitrate modified biochar at 400°C. The intensities of the peaks vary with precursors indicating that pristine biochar reacted differently with the precursors. Figs. 3–5 show the high-resolution
mass spectral images for the three aforementioned samples. The overlaid images exhibit green color which suggests that nitrogen was successfully doped in the biochar matrix. The mass spectrometry data and spectral images for pristine biochar and melamine modified biochar at 400 °C are provided in the associated manuscript [1].

Figs. 6–10 show the electron map images of the elements detected in pristine biochar, melamine, ammonium chloride, ammonium nitrate, and urea modified biochars at 400 °C respectively obtained by SEM-EDX. The associated SEM images and EDX spectra for the sample in the linked manuscript [1]. Table 1 shows the surface profile data of the biochar samples prepared at 400 °C at 480× magnification. The attached ‘profilometry’ spreadsheet has laser optical images of the biochar along with their profile graphs at different magnifications.
Fig. 2. Negative ion ToF-SIMS spectra for ammonium chloride (top), ammonium nitrate (middle), urea (bottom) modified biochar samples at 400°C.

2. Experimental Design, Materials and Methods

2.1. Sample preparation

Pine bark nuggets were obtained locally in NC, USA. These nuggets were pyrolyzed in a box furnace at a heating rate of 10°C min⁻¹ under N₂ flow (5 L min⁻¹) up to 400°C and main-
Fig. 3. ToF-SIMS original and overlaid images of negative ions in ammonium chloride modified biochar at 400°C (CBC). The original images are shown for all the observed ions. Overlaid images are shown for and C$_3$N$^-$ ions on C$_6$H$^-$ ion.
Fig. 4. Tof-SIMS original and overlaid images of negative ions in ammonium nitrate modified biochar at 400 °C (NBC). The original images are shown for all the observed ions. Overlaid images are shown for and C$_3$N$^-$ ions on C$_6$H$^-$ ion.
Fig. 5. Tof-SIMS original and overlaid images of negative ions in urea modified biochar at 400 °C (UBC). The original images are shown for all the observed ions. Overlaid images are shown for and $\text{C}_3\text{N}^-$ ions on $\text{C}_6\text{H}^-$ ion.
tained for 4 h. The pristine biochar so obtained was produced which was then ground and sieved (<200 mesh).

Nitrogen modified biochar samples were produced by mixing 10 g of pristine biochar with 1 g of nitrogen, from either of the four studied precursors, in 50 mL of deionized water. Thus, 2.14 g urea (≥ 99%, CAS: 57–13–6, Fisher Scientific), 1.50 g melamine (99%, CAS: 108–78–1, Acros Organics), 3.82 g ammonium chloride (99%, CAS: 12,125–02–9, Acros Organics), and 2.85 g
ammonium nitrate (≥ 99%, CAS: 6484–52–2, Sigma-Aldrich) were used to produce nitrogen-doped biochars. The obtained slurry was heated at different temperatures (400–800 °C) for 1 h.

2.2. Scanning electron microscopy (SEM)

Biochar samples were sputter-coated (Hummer II, manufactured by Anatech) with Au for 5 min @ 7 nm/min after sticking them on the sample stub. Subsequently, surface morphology and chemical composition data were collected using a Hitachi S3200 N variable pressure SEM via a 20 keV electron beam for imaging an EDX.

2.3. Time of flight-secondary ion mass spectroscopy (ToF-SIMS)

ToF-SIMS analyses were conducted using a TOF SIMS V (ION TOF, Inc. Chestnut Ridge, NY) instrument equipped with a Biₙⁿ⁺⁺ (n = 1 – 5, m = 1, 2) liquid metal ion gun, Cs⁺ sputtering gun
(both angled at 45° to the sample surface normal) and electron flood gun for charge compensation. The analysis chamber pressure was maintained below $5.0 \times 10^{-9}$ mbar. For high mass resolution spectra acquired in this study, a pulsed Bi$^{3+}$ primary ion beam at 25 keV impact energy with less than 1 ns pulse width was used. High lateral resolution mass spectral images of biochar samples were acquired using a Burst Alignment setting of 25 keV Bi$^{3+}$ ion beam. The negative secondary ion mass spectra obtained were calibrated using C$^-$, O$^-$, OH$^-$, C$_n$$^-$, respectively.

2.4. Surface profilometry

A confocal laser scanning microscope (CLSM, Keyence VKx1100) was used to study the surface profiles of the powdered biochar samples. CLSM provides the 3-D optical images as well as the surface roughness of the materials using optical microscopy, laser (404 nm violet laser and white light as excitation sources) profilometry, and the multifile analyzer software.

2.5. Infrared spectroscopy

To collect the data on the surface functional groups formed on the biochar samples, infrared (IR) spectra of the powdered biochar samples were acquired using a Bruker Platinum ATR spectrometer. Powders were placed such that the sample compartment was coated completely. The IR spectral data were collected for a range of 400–4500 cm$^{-1}$. Subsequently, the raw data thus collected were plotted using Origin software (OriginLab Corporation, USA).

CRediT Author Statement

Nitesh Kasera: Conceptualization, Methodology, Data Collection, Writing – Original draft preparation; Steven Hall: Supervision, Writing – Reviewing and Editing; Praveen Kolar: Conceptualization, Investigation, Supervision, Writing – Reviewing and Editing.
Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships which have or could be perceived to have influenced the work reported in this article.

Acknowledgments

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Reference

[1] N. Kasera, P. Kolar, S. Hall, Effect of different nitrogen precursors on morphology and surface chemistry of pine bark biochar, J. Environ. Chem. Eng., doi: 10.1016/j.jece.2021.105161.