Biochar for Sustainable Resource Recovery and Remediation

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Environmental and Remediation

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Session 3A Biochar 2018,
Waste for contaminant immobilization and resource recovery?

Sewage Sludge/Urban Waste

Agricultural Waste

Biomass

Plastics
Technologies for Feedstock Conversion

Pyrolysis (Biochar)
- Gas Input
- Temperature Monitor & PID Control
- Heating Coil
- Coolant in
- Coolant out
- Gas Egress

Hydrothermal (Hydrochar)
- Temperature & Pressure Monitor & PID Control
- Pressure Vessel & Safety Disk
- Sub-Critical Water
- Heating Coil

Char
Composite Carbon Materials
Composite Carbon Materials – Sustainable Applications

Energy Production:
- Pyrolysis & Gassification
- Advanced Combustion

Waste Management:
- Sustainable waste disposal
- Bioenergy from wastes

Climate Change Mitigation:
- Soil Carbon Sequestration
- Bioenergy production

Agriculture & Horticulture:
- Soil Improvement
- Land Remediation
- Livestock Feed

Sorbents & Remediation:
- Land Remediation
- Toxic cleanup
- Recovery of precious material

Manufacture & Other uses:
- Fuel Cells
- Catalysis
- Building Materials
- CO2 sequestration etc etc…
Understand the fundamental chemical properties of chars

**What is the Carbon chemistry of chars?**

**Biochar**
- Mostly aromatic carbon, including *electron shuttles* (e.g., quinones)
- Surface vs. bulk chemistry may be very different.

**Hydrochar**
- High Molecular Mass
- Complex Oils on Surface

Energy Loss [eV]
Surface Carbon Chemistry

~ 30 - 40 nm spatial resolution
Bulk Carbon Chemistry

X-ray Raman scattering technique embodies all the advantages of hard X-rays and yields information typically obtained by soft x-ray (NEXAFS)

\[ \theta = q = k_1 - k_2 \]

The Sample

![Graph showing energy loss vs. intensity with peaks at different energies labeled as Phenolic, ERF, C=O (Furan), Quinonic, Alkyl, and Aromatic.](image)
Comparing Biochar and Hydrochar Carbon Chemistry

<table>
<thead>
<tr>
<th>Energy in eV</th>
<th>Biochar Peak area</th>
<th>Hydrochar Peak area</th>
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<tr>
<td>284.8</td>
<td>0.79</td>
<td>0.81</td>
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<td>285.3</td>
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<td>287.3</td>
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<td>0.81</td>
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<tr>
<td>288.2</td>
<td>0.62</td>
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<td>289.3</td>
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<tr>
<td>290.4</td>
<td>0.68</td>
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X-ray Absorption Spectroscopy for Fe and S Chemistry

Determines:
1) effective oxidation state
2) detailed coordination environment
- Biochar has mixed Fe(II/III) species.

- Mixed Fe(II/III) oxides are strong reductant. (e.g., Magnetite)

- Biochar can reduce and immobilize many contaminants or recover resources.
Sulfur Chemistry of Biochar

S moieties on Biochars include sulfhydryl groups.

**S XANES Standards**

**S XANES of Biochar**

[Graphs showing X-ray fluorescence yield and normalized X-ray absorption spectra for different sulfur species and biochar samples.]
Inherent Redox Properties of Biochar

- Electron shuttling capabilities.
- Mixed Fe(II/III) oxides i.e., reductants
- Sulfhydryl groups i.e., reductant/oxidant and complexing agent
- Most contaminants (heavy metals) could be easily reduced to less harmful forms (i.e., Cr, U, Hg).

How can we enhance chemical properties of Biochar?
What are the drivers of Biochar Chemistry?

Can we modify surface complexation properties of chars?

- **Synthesis Condition**
  - Aromaticity
  - Functionality
  - Stability

- **Starting Material**
  - Porosity
  - Morphology
  - Inorganic Chemistry

**The Shell Model**
Functionalized Engineered Biochar from Our Group

- We impregnate biochar surface with minerals (e.g., MgO/MnO$_2$) and functionalize them with ligands (e.g., thiols, amines).

Route to Produce “functionalized” Biochar

MgO nanoparticulate on surface confirmed by XRD and TEM.
Recovery of Gold from Industrial Waste Water?

Industry Waste Water

$\text{Au}^{3+} \text{Cl}_3$

$\text{Au}^0$

Resource Recovered

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<th>Model</th>
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<td>Reduced Chi-Sqr</td>
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<td>R-Square (COD)</td>
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<td>Adj. R-Square</td>
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Experimental Set-up for Metal Uptake & Analyses

Oak Wood Biochar - 650

Gold(III) Chloride AuCl₃

Wash Solution

Centrifuged filtered & washed

Solid Phase

Liquid Phase

Flame – AAS & ICP-MS

45 mins

S/TEM

XAFS

Radial Distance [Å]

BC-Au200
BC-Au500
BC-Au1000
BC-Au2500

Gold (Au) Signal
Carbon (C) Signal

HAADF image
Overlay of elements

Data Processor

Graph showing |F(R)| vs Radial Distance [Å] with peaks at Au - Au and Au - Cl.
TEM Characterization of Au on Biochar

- TEM confirmed the presence of Au NP.
- Au was distributed both on the surface and within the biochar.
- Average visible Au NP size was around ~10nm.
- Interestingly, many of the Au NP were located next to Fe oxides in the biochar.

STEM EDX imaging of a porous char particle after adsorption of gold onto the surface. Gold can be seen as a red colour, whilst carbon can be seen in green.
Fe ELNES using TEM

- A film of Fe Oxide surrounds Au nanoparticle.
- Fitting ELNES data showed a change in redox state for Iron oxide.

\[
\text{Au(III)} + 3\text{Fe}^{2+} \rightarrow \text{Au}(0) + 3\text{Fe}^{3+}
\]

Position

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<th>Hedenbergite (Fe$^{2+}$)</th>
<th>Haematite (Fe$^{3+}$)</th>
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<td>Distant</td>
<td>44%</td>
<td>52%</td>
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<tr>
<td>Adjacent</td>
<td>67%</td>
<td>38%</td>
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Hedenbergite (Fe$^{2+}$) Haematite (Fe$^{3+}$)
Au EXAFS confirmed Au NP.

Three different mechanisms (Fe, C, S) responsible for Au redox transformations.

EXAFS average NPAu size 3-4 nm; smaller than observed by TEM.

~20 weight% capacity of Biochar to recover Au as NP.
Sensitivity for CN vs. Particle Size
Au edge EXAFS

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<th>Calculated</th>
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<th>Observed</th>
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</table>

1 nm  
2 nm  
3 nm  
5 nm
Mechanisms Responsible for Au Transformations

- Evidence for the reduction by mixed Fe(II/III) Oxides

- Electron shuttling by Carbon moieties on in the biochar (e.g. Quinone)

- Intermediate speciation such as Au(I)S??

Image elements:
- Amorphous carbon – pyrochar particle
- nAu inside a carbon pore
- Mineral phases

Scale: 200 nm
Summary

- Biochar and Hydrochar can be created from biogenic waste (e.g., Urban and Agricultural Waste)

- Biochar have inbuilt reductive and electron shuttling capabilities.

- In addition, they could be engineered for enhanced uptake of specific contaminants and resources, and transform them as desired.

- Applications include water treatment, waste management, and resource recovery (e.g., recovery of Au from industrial waste water).

- If converted to real time use, this could be first step towards truly circular economy and sustainable society.
Acknowledgement

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Email:  b.mishra@leeds.ac.uk
Conceptual Design of Distillation and Nano-filtration Harnessing Solar Energy

Schematic not to scale
Conceptual Design...continued

**Phase I**
- **Distillation**
  - Engineered glass
  - Contaminated water
    - Inorganic & organic contaminants, bacteria, particles
  - Distillation → sterilization
    - Volatilization of certain organics

**Phase II**
- **Filtration**
  - Engineered bio-products
    - Algae 1
    - BioChars, HydroChars 2
    - Biogenic Minerals 3
    - Biopolymers 4
  - Sorption, redox chemistry, co-precipitation, nano-filtration → Immobilization

**Volatilization of certain organics**

One PhD student working on each of these aspects in my group.
What do we do with biogenic waste?

- Biogenic waste from various sources
- Landfill -> GHGs
- Generally combusted for EfW -> no products
- Can we develop functional material out of it?
Carbon Chemistry X-ray Raman Standards with Soft X-ray

X-ray Raman and C NEXAFS compared

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<tr>
<th>Standard</th>
<th>Peak energy this study</th>
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<tr>
<td>p-Benzoquinone</td>
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