Retention and plant bioavailability of urine derived nutrients by biochars

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Presentation Overview

- Reinventing the Toilet Challenge
- Literature review of ammonia sorption
- Experimental Methods
- Results and Discussion
- Conclusions – Application?
- Other biochar work with the Toilet project
- Future work
The Problem

▪ 2.5 billion people around the world lack access to basic sanitation (40% of global population)

▪ 1.1 billion people defecate in the open

▪ At current rates of progress, the world is set to miss the MDG target for sanitation by over half a billion people

▪ Safe management of fecal sludge is a major challenge for rapidly urbanising developing country populations

Kibera, Kenya
The Current Approach

- Dry pit latrine or a VIP (most common form of on-site sanitation)
- Composting toilets
  - Fills quickly
  - Difficult to remove waste
  - Transportation of removed waste poses additional risks to public health and the environment
- Or – the western approach derided by Liebig as “The Irresistible Flush”
  - Turns nutrients into contaminants
  - Requires large amounts of increasingly scarce water
  - Expensive and energy intensive
Our Approach: The Sol-Char Toilet take this sanitation value chain...
...and reduces it to this:

While creating usable products
Without grid energy, water, sewer
**Sol-Char Toilet**

Parabolic dishes concentrate solar energy

Fiber optics transmit energy to a high temperature reactor

Reactor thermally inactivates human waste

Useful end products are created
Urine Diversion

- More effective use of solar thermal energy than mixed waste
- Healthy urine is sterile when excreted
  - However it is easily fecally contaminated
- Simpler separation at the source rather than after mixing
- 90% of the nutrients in human waste are in urine
  - Easier captured when separated
Urine Background

- High concentrations of N, P, K among other nutrients
- Initially, nitrogen is in the form of urea
- Rapidly, urea converts to ammonia through a biological process
- Other compounds precipitate
- This ureolysis causes:
  - Phosphate and calcium to precipitate
  - A drastic increase in pH

Urine Background

- ~89% of nitrogen in fresh urine is in the form of urea
- Rapidly converted to ammonia (in conditions with ANY biological activity, minutes to hours)

\[
(NH_2)_2CO + H_2O \xrightarrow{\text{urease}} CO_2 + 2NH_3
\]

- Ammonia speciation with Ammonium:
  
  \[
  NH_4^+ \xleftrightarrow{pK\alpha=\sim9.2} NH_3 + H^+
  \]
  
- Typically stored urine has a pH around 9.0

The potential exists to capture nutrients in urine (most likely ammonia) out of the urine stream

- Creates an added value for the nutrient enriched biochar
- Addresses the concerns for ammonia odor during storage of urine in the toilet area & during land application of urine (if applicable)
- Can be an important part of a total nutrient recovery system for a compound which will not precipitate

- These compounds commonly become contaminants in traditional sewered wastewater treatment outfalls
Urine Filtration through Biochar

- Adsorption of ammonia with biochar has been demonstrated by Asada et al., 2006; Taghizadeg et al., 2012; and Day et al., 2005)
  - HOWEVER this is always shown either in the gas phase or under low concentrations in a pure DI water matrix
  - Additionally, the applications for these studies very greatly from this our sanitation and agricultural paradigm
    - Including removal of ammonia in drinking water before the addition of chlorine to avoid the formation of chloramines
    - Addressing the problem of Sick Building Syndrome and odors in building ventilation.
    - Avoiding volatilization of ammonia in soil

<table>
<thead>
<tr>
<th>Carbon Use Rate</th>
<th>Investigators</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 to 6 mg/g</td>
<td>Asada et al., 2006</td>
</tr>
<tr>
<td>7.8 to 10.0 mg/g</td>
<td>Taghizadeh-Toosi et al., 2011</td>
</tr>
<tr>
<td>2.4 to 5.9 mg/g</td>
<td>Taghizadeh-Toosi et al., 2012</td>
</tr>
<tr>
<td>Up to 60 mg/g</td>
<td>Seredych &amp; Bandosz, 2007</td>
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</table>
Explicit studies in a urine matrix are needed because it is the only way to reproduce important factors to the adsorption of ammonia

- High ammonia concentrations from 4, to 9 g/L (orders of magnitude above current studies)
- High salt content in urine
- Variety of competing constituents including organics
- Ambient pH effects on biochar surface reactions
- Buffering capacity of a urine matrix and its reactions with biochar surface
Methods – Synthetic Urine

- Synthetic urine generated from recipe by EAWAG
- pH altered by NaOH or H₂SO₄
- Verified to be stable in storage with controls

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Concentration [g L⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SO₄ anhydrous</td>
<td>2.30</td>
</tr>
<tr>
<td>NaH₂PO₄ anhydrous</td>
<td>2.10</td>
</tr>
<tr>
<td>NaCl</td>
<td>3.60</td>
</tr>
<tr>
<td>KCl</td>
<td>4.20</td>
</tr>
<tr>
<td>NH₄Ac</td>
<td>9.60</td>
</tr>
<tr>
<td>25% NH₄OH solution [mL·L⁻¹]</td>
<td>13.0</td>
</tr>
<tr>
<td>NH₄HCO₃</td>
<td>21.40</td>
</tr>
</tbody>
</table>

Methods - Batch & Column Studies

- Batch studies to find capacity for chars to remove urine
  - Kinetic study: To evaluate the transfer rate of ammonia sorption and to inform appropriate batch mixing times
  - Dose-Response experiments with a wide variety of chars and varying matrix conditions

<table>
<thead>
<tr>
<th>Furnace (retort) Wood Biochars</th>
<th>Gasifier Wood Chars</th>
<th>Alternative feedstocks</th>
</tr>
</thead>
<tbody>
<tr>
<td>· Bamboo at 350C</td>
<td>· Pine at 900C (TLUD FD)</td>
<td>· Fecal sludge at 300C (retort)</td>
</tr>
<tr>
<td>· Bamboo at 900C</td>
<td>· Pine at 600C (TLUD ND)</td>
<td>· Rice Husk Gasifier ~800C?</td>
</tr>
<tr>
<td>· Pine at 900C</td>
<td></td>
<td>· Powdered Activated Carbon</td>
</tr>
</tbody>
</table>
Methods - Batch Studies

- Conducted in 50mL centrifuge tubes
  - Duplicate samples with 10mL liquid urine sample with 2 to 8 grams of biochar – forming a slurry
- Biochars ground and sieved to pass No. 100 (0.152 mm)
- Place in tumbler for 24 hours to ensure complete mixing and allow mixture to reach equilibrium
- Remove samples and filter through GF-C vacuum
- Test pH and tNH₃ levels for samples and controls

\[ t\text{NH}_3 \] measures total ammonia (NH₃) plus ammonium (NH₄⁺)

HACH TNTplus method 832 (http://www.hach.com/ammonia-tntplus-uhr)
Batch Kinetic Study

- Confirming that ammonia adsorption is a rapid process
- 24 hour sampling time selected as this is well after equilibrium
Selection of Biochar/carbons

- Powdered Activated Carbon (PAC)
  - Industrial standard for sorption media

- Rice Husk Gasifier Char
  - Char residual from cookstove (Olivier, P.)

- Top-Lit-Up-Draft (TLUD) Pine 600C
  - TLUD gasifier cookstove under natural draft

- TLUD Pine 900C
  - TLUD gasifier cookstove under forced draft

- Pine 900C, Bamboo 900C, Bamboo 300C, Fecal Sludge 300C
  - Retort char from a temperature controlled furnace
Ammonia Removal Batch - pH ~9.3 [normal urine]

% Ammonia Captured

Carbon (biochar) Dose, g/L

- PAC
- Rice Husk
- TLUD Pine 600C
- TLUD Pine 900C
- Pine900C
- Bamboo900C
- Bamboo 350C
- Fecal Sludge 300C
Ammonia Removal Batch - pH ~9.3 [normal urine]

Capacity: 3 to 5 mg N per g char

- PAC
- Rice Husk
- TLUD Pine 600C
- TLUD Pine 900C
- Pine900C
- Bamboo900C
- Bamboo 350C
- Fecal Sludge 300C
Results

- Biochar feedstock or charring temperature/method does not play a major role in terms of sorbing nitrogen
  - Most chars have an NH₃ uptake between 3 and 5 mg/g carbon
  - Fecal sludge biochar performs comparable including PAC – Surface area not a factor

- pH change appears to be a factor

<table>
<thead>
<tr>
<th>Biochar Type</th>
<th>Removal at dose 600g/L</th>
<th>NH₃ Uptake (mg/g carbon)</th>
<th>BET Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAC</td>
<td>56%</td>
<td>4.6</td>
<td>700</td>
</tr>
<tr>
<td>Pine 900 (gasifier)</td>
<td>61%</td>
<td>4.4</td>
<td>480</td>
</tr>
<tr>
<td>Pine 900</td>
<td>***</td>
<td>3.3</td>
<td>360</td>
</tr>
<tr>
<td>Bamboo 900</td>
<td>50%</td>
<td>3.9</td>
<td>310</td>
</tr>
<tr>
<td>Pine 600 (gasifier)</td>
<td>44%</td>
<td>4.11</td>
<td>270</td>
</tr>
<tr>
<td>Bamboo 300</td>
<td>***</td>
<td>5.4</td>
<td>210</td>
</tr>
<tr>
<td>Fecal Sludge</td>
<td>39%</td>
<td>4.2</td>
<td>1</td>
</tr>
</tbody>
</table>
pH = 10.3 vs. pH = 9.3

% Captured in Biochar vs. Carbon Dose (g/L)

- pH = 10.3: Data points at 200, 400, and 600 g/L, with captured percentages of 10%, 20%, and 30% respectively.
- pH = 9.3: Data point at 300 g/L, with a captured percentage of 50%.

9.3 Fecal Sludge 300
pH effect on removal
Change in pH - Results

- At pH=10.3, 90% of tNH₃ in the form of NH₃ higher concentration is felt by the surface from the solution
- Confirms that Ammonia NH₃, is preferably removed  
  - Because higher removals achieved at higher pH
- Higher pH batch shows some differences in char type  
  - Low temperature bamboo performs the best  
  - This char also altered the pH of the water downward from 10.3 to 9.5
- Neutral particle (NH₃) is removed more than cation (NH₄⁺) indicating not ion exchange sorption mechanism
- Clearly a pH dependent sorption mechanism is at play

<table>
<thead>
<tr>
<th>% captured at 400 g/L dose</th>
<th>pH = 8.3</th>
<th>pH = 9.3</th>
<th>pH = 10.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bamboo 350</td>
<td>22%</td>
<td>35%</td>
<td>75%</td>
</tr>
<tr>
<td>Bamboo 900</td>
<td>28%</td>
<td>19%</td>
<td>50%</td>
</tr>
</tbody>
</table>
Column Experiment

- Bamboo at 350C
- EBCT = 19m
- Synthetic urine pH=10.2
- Minor initial pH change to 9.8
- Cumulative capacity 6mg/g

Contact Time = 19 min.
Pre-Loaded Biochar Application

- Ammonia sorbed biochar previously shown to be bioavailable (Taghizadeh-Toosi et al., 2012)

- Biochar capacity to hold ammonia confirmed at 3 to 6 mg/g in batch and flow-through experiments

- Assuming the capacity from the batch study: 6 mg N / g char (metric ton/hectare)

- And a low crop nitrogen requirement based on Zambia study (Cornellison, 2011)

- Char can satisfy nitrogen fertilizer requirements

<table>
<thead>
<tr>
<th>N fertilizer requirement</th>
<th>Char Required to meet N requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 kg N/he</td>
<td>3.3 m. tons/he</td>
</tr>
<tr>
<td>17.8 lbs/acre</td>
<td>3,500 lbs/acre</td>
</tr>
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</table>
Conclusions

- Nitrogenous nutrients can be captured from a urine stream using biochars
  - Likely through complex and pH dependent acid-base reactions on the surface of the carbon
  - Need a LOT of char to hold it all

<table>
<thead>
<tr>
<th>To get ALL nitrogen out of 1L of urine:</th>
</tr>
</thead>
<tbody>
<tr>
<td>9gN/L in urine</td>
</tr>
<tr>
<td>0.006gN/gChar Capacity</td>
</tr>
<tr>
<td>1500gChar for one liter of urine</td>
</tr>
<tr>
<td>300g/L Char Density</td>
</tr>
<tr>
<td>5Liters of Char</td>
</tr>
</tbody>
</table>

- Ammonia (NH₃) appears to be preferably removed over Ammonium (NH₄⁺) in a urine matrix
- Capacity of all biochars is capable of being used as a mechanism to field-apply fertilizer
- Urine pH can be raised in to achieve ~20% improved capture of ammonia
- Biochar with a lower pH and PZC can achieve slightly higher ammonia capture
Other Biochar Investigations
Odor Suppression of Urine

▪ Urinal constructed with biochar filter at top
▪ 65g Pine biochar (900C) Filter
▪ Suppressed urine odor for 7 days
  ▪ Ammonia/urine odors were not detectable to the nose

<table>
<thead>
<tr>
<th>Biochar Filter Life:</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.2g Char / L urine</td>
</tr>
<tr>
<td>9.3g Char / day</td>
</tr>
</tbody>
</table>

▪ Repeat tests will be quantified with Ammonia gas meter
Human Waste Drying Odor Removal

Drying-phase Odor Measurement

- Before Biochar
- After Biochar

Upper Detection limit is 500 ppm

I smell bad!
Future work

▪ Further investigate other ways to recover nutrients
  ▪ All NPK through urine fertilizer application (business model)
  ▪ Phosphorus
    ▪ Precipitation in urine
    ▪ Bioavailability in fecal sludge biochar
  ▪ Potassium
    ▪ Recovery as potassium magnesium phosphate in precipitate

▪ Research the impact of biogrowth in a filter column

▪ Conduct pilot scale evaluations of biochars’ potential role in addressing odor of exhaust and urine/feces bathroom smells

▪ Incorporate urine nutrient sorption into business model and further develop operational parameters
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Sol-Char Toilet

Thank You
Teams

- 16 Reinvent the Toilet Teams
- Novel Idea Examples:

- **RTI**: Electrochemical disinfection and solid waste combustion
  - [www.rti.org](http://www.rti.org)

- **Cranfield**: Nanomembrane toilet
  - [http://nanomembranetoilet.org/blog.php](http://nanomembranetoilet.org/blog.php)

- **Caltech**: Electrochemical chemical cell (for liquid treatment)
  - [www.impatientoptimists.org](http://www.impatientoptimists.org)

- **TU Delft**: Gasification of via microwave plasma discharge
Biochar Optimal Production Conditions

- Currently we are confident in proceeding with production temperatures in the 400-500ºC range
  - There is little to no agricultural or solid fuel benefit in reaching higher temperatures
    - Exception: surface area does increase at higher temperatures (>750ºC) which may be beneficial if poo-char is used in odor removal applications
  - This production range is high enough to drive off some tars which cause product removal difficulties at lower temperature (<=350ºC)
  - This range does not challenge the materials used in the reactor
    - Fused fiber bundle: 600ºC – Max temp before glass transition of silica (glass creep). This change in material properties may change the optical properties.
    - Fiber cladding and epoxy: 300ºC – Max temp before fiber cladding or epoxy melts. This is the max temperature at the outer wall of the solar lid. This may not be an issue with convective cooling, fused fiber ends, or quartz rod interfaces.
    - Stainless steel reactor: 899ºC – Max temp before material changes occur however intermittent heating above 816ºC is not recommended.

- The time required for charring will be dependent on achieving production temperature throughout the waste (once temperature is achieved, pyrolysis is a rapid process)
  - Experiments will be conducted to identify and avoid cold spots in the reactor and to establish the time required to achieve total pyrolysis
Thank You

Like us on facebook!
http://www.facebook.com/SolarBiochar
Biochar with strongest sorbability does have lowest PZC (Bamboo at 350C with 8.1).

However at the ambient pH of urine, this makes the surface negative.
  - A negative surface should attract positive NH4+ better if ion exchange were occurring.

Shows that ion exchange is not the mechanism.
Biochar Characterization as an Agricultural Product or Solid Fuel

For more detailed information about previous data collected please see previous progress reports.

Only new data and activities presented here.
- Study achieving 60 mg/g sorption capacity used
- Graphite oxide – which is more regular graphene sheet structure with oxygen functional groups
### Results

- Data has been previously collected which informs all of the following important parameters

<table>
<thead>
<tr>
<th>Property</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Longevity in soils</td>
<td>Potential for CO2 sequestration, durability of benefits</td>
</tr>
<tr>
<td>2. Cation Exchange Capacity (CEC)</td>
<td>Retention and bioavailability of inputs (e.g. N, P, K fertilizers)</td>
</tr>
<tr>
<td>3. pH / Liming Effect</td>
<td>pH balance &amp; buffering, Al toxicity</td>
</tr>
<tr>
<td>4. Structure</td>
<td>Accumulation of organic material, biofilm establishment, retention of inputs and H₂O</td>
</tr>
<tr>
<td>5. Nutrient content</td>
<td>Bioavailability of nutrients in the product</td>
</tr>
</tbody>
</table>

**Fertilizer / Compost / Biosolids Tests**
Other Biochar Uses

▪ Pre-loading with nutrients from urine
  ▪ Found that it is possible to remove > 50% of nitrogen from urine using biochar from fecal sludge
  ▪ Comparable to other types of biochar

▪ Limiting odors associated with urine storage
  ▪ In small pilot unit testing found that 9 grams of char is required per day for odor suppression

▪ Adsorbing odors from drying of human waste
  ▪ 100% Removal of Hydrogen Sulfide
  ▪ Water vapor and tars/oils were condensed before treatment